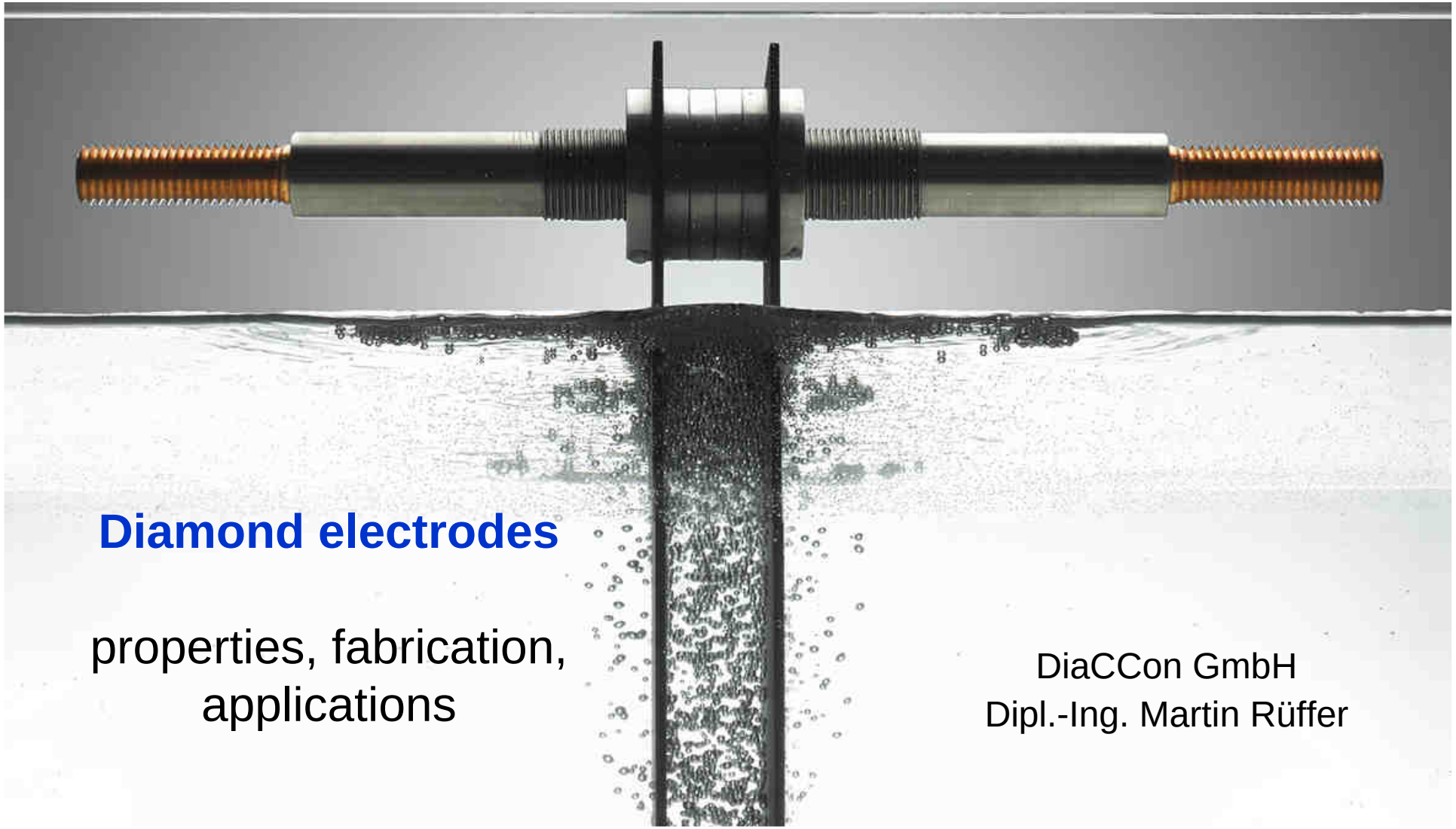
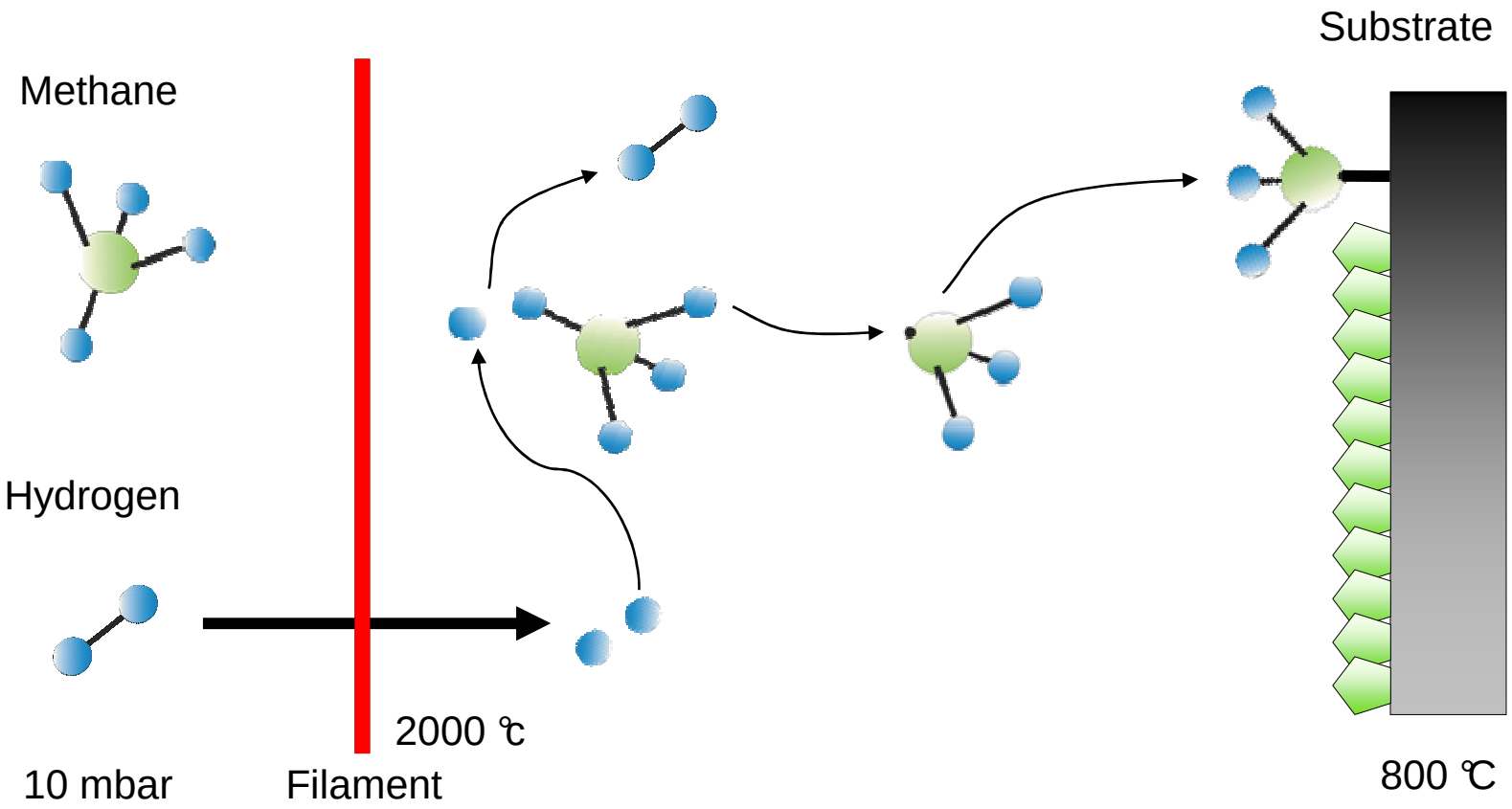


Diamond electrodes

properties, fabrication, applications

DiaCCon GmbH
Dipl.-Ing. Martin Rüffer

How to make diamond

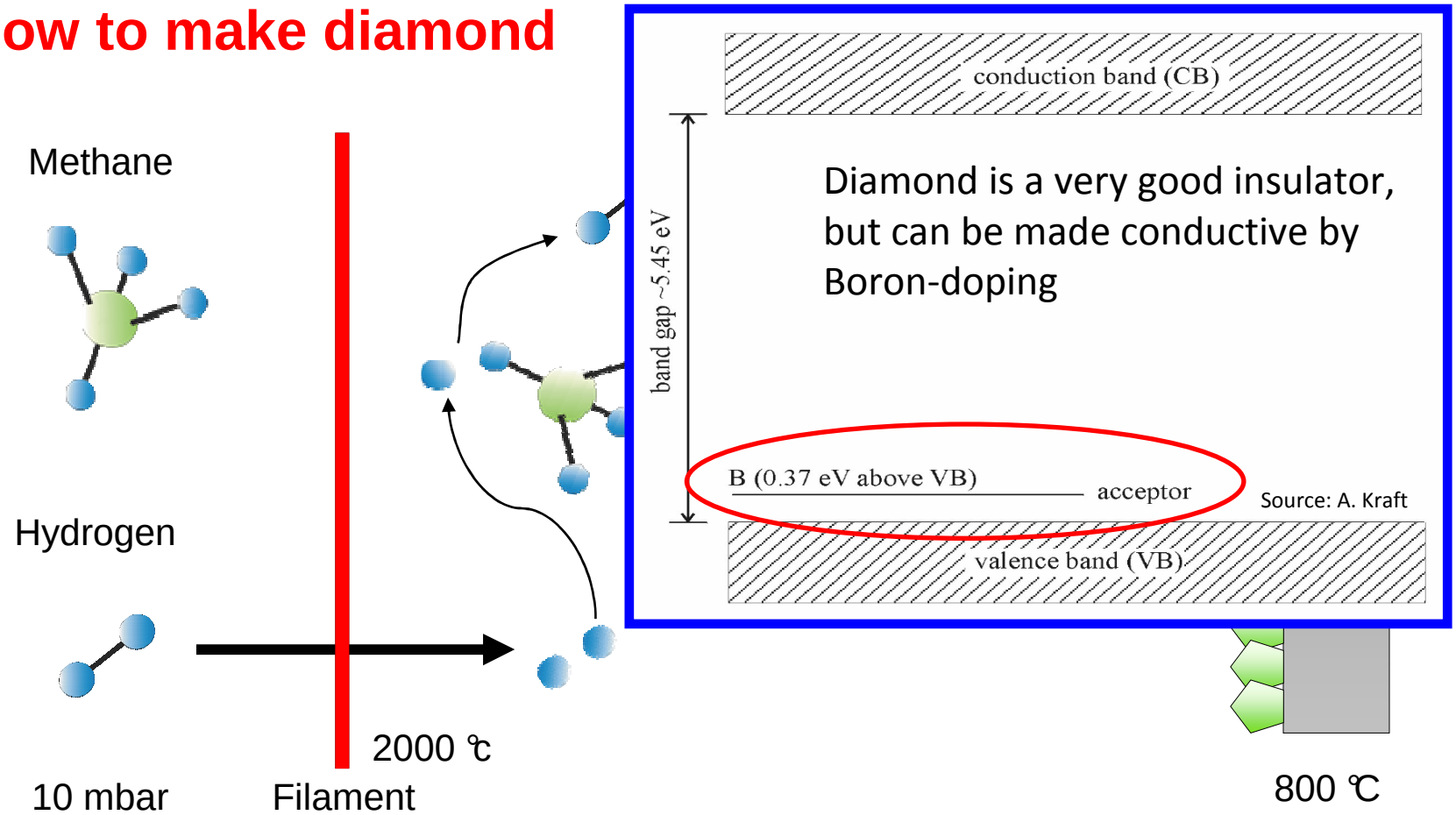


Generation of radicals

deposition of diamond

Basic setup

How to make diamond



Diamond is a very good insulator, but can be made conductive by Boron-doping

Generation of radicals

deposition of diamond

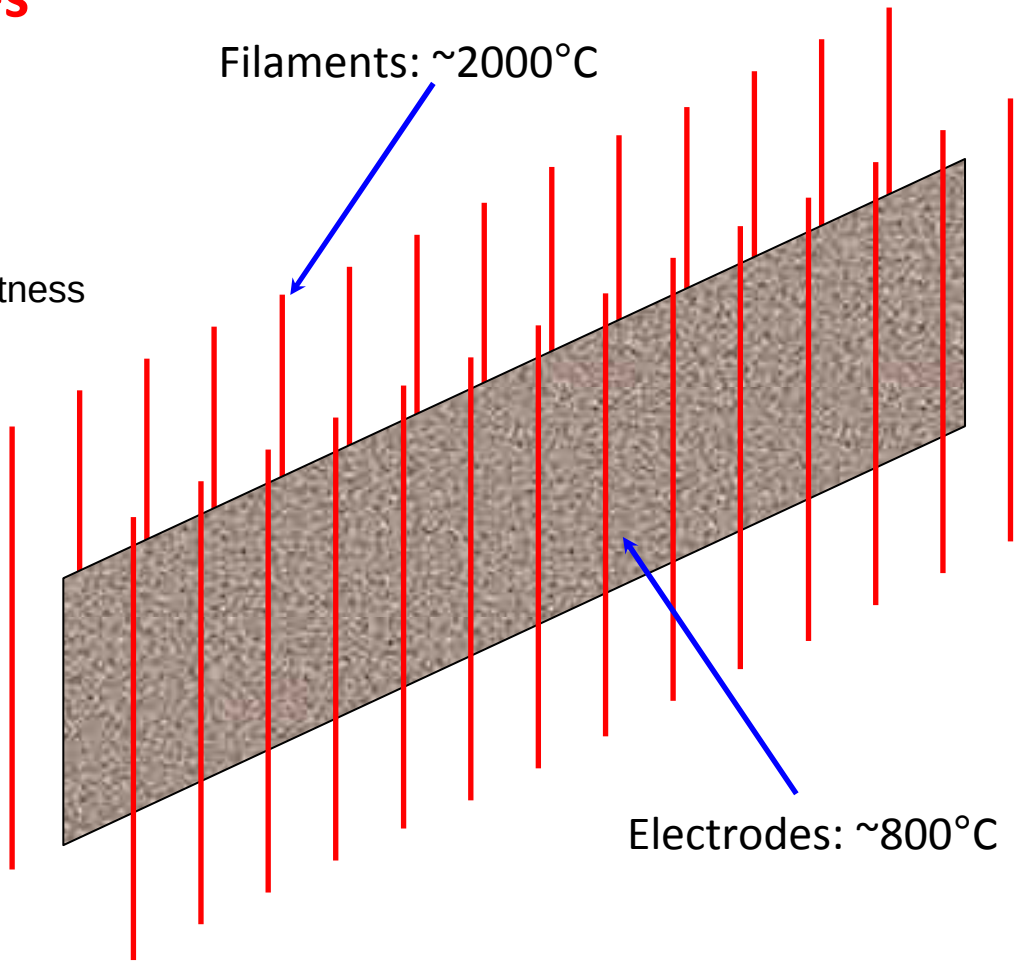
Basic setup

Setup for coating electrodes

Toaster-Principle

Vertical filaments enclosing the substrate

Ensure homogeneity of temperature and flatness



Standard coating thickness is 12µm for excellent longterm stability

Production equipment

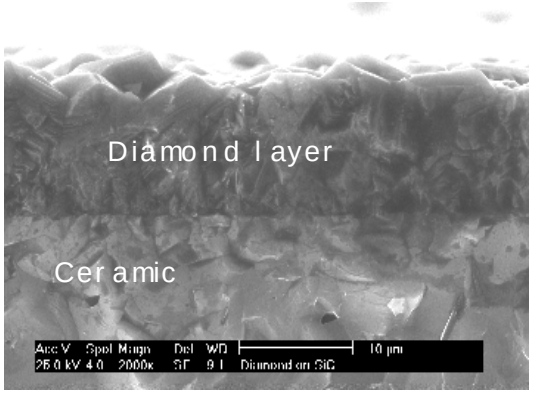
-Three of probably worlds largest diamond-machines

-Very close cooperation with manufacturer of these machines

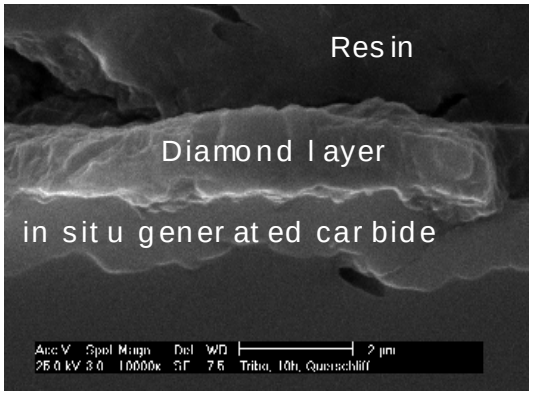
-Professional technology and equipment

Coat able materials

Ceramics / Silicon



Metals



-Very good adhesion by chemical bonding of coating to substrate

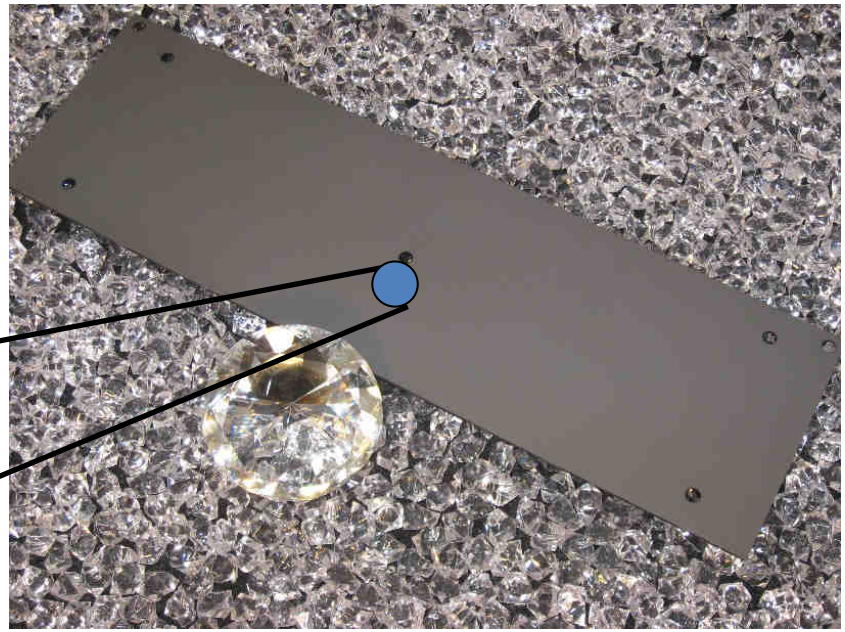
	II										III	IV
Li	Be										B	C
Na	Mg										Al	Si
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Ga	Ge
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	In	Sn
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Tl	Pb
	Ra	Ac										

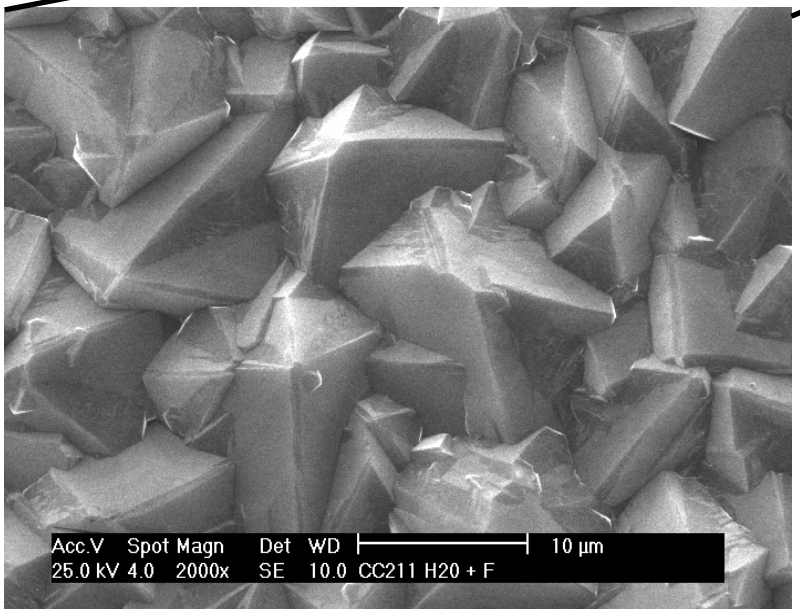
- very good coatable (strong adhesion)
- coatable
- uncoatable (generation of graphite)

The Diamonds…

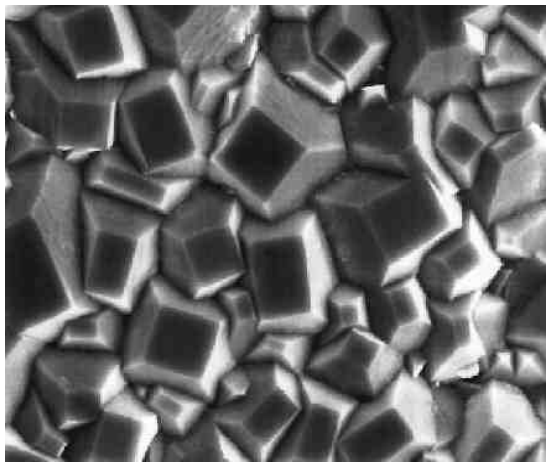
Morphology can be influenced by:

-gas composition
-gas flow
-gas pressure
-substrate temperature
-filament temperature
-etc.

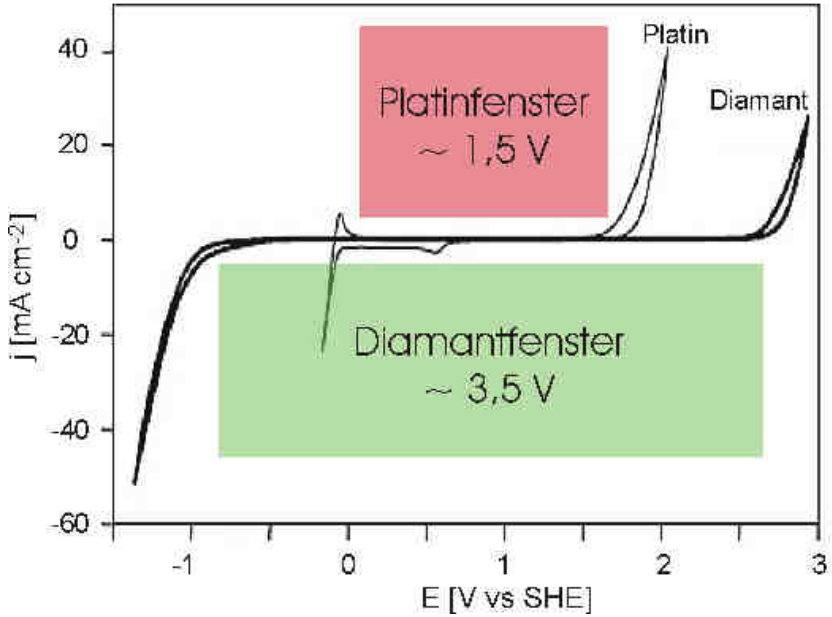




Various morphologies



Different electrode materials in comparison



-high overpotential for oxygen and hydrogen evolution in aqueous media

-reason is the limited interaction/adsorption of water to the diamond

-high energies are required:

$\triangle$G [hydrogen]: 150kJMol^{-1}

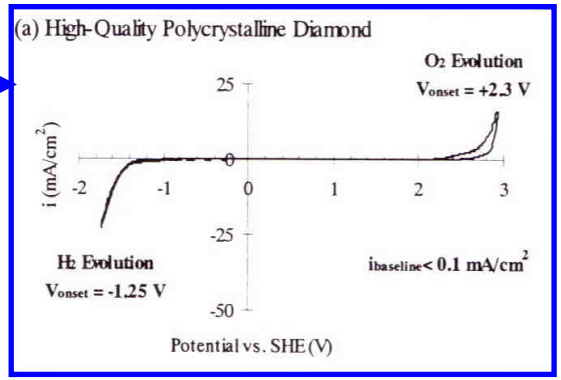
$\triangle$G [oxygen]: 106kJMol^{-1}

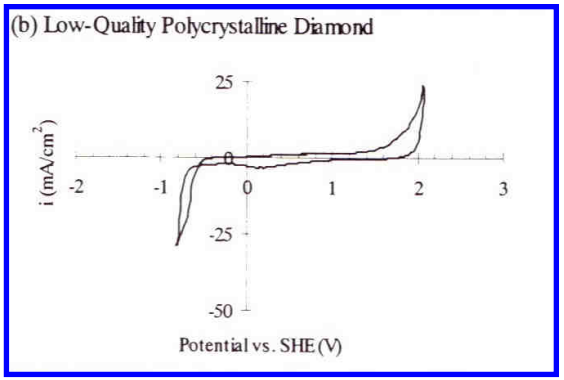
In comparison for platinum:

$\triangle$G [oxygen]: 47kJMol^{-1}

Source: Hugo B. Suffredini

Size of potential window can be influenced by diamond quality

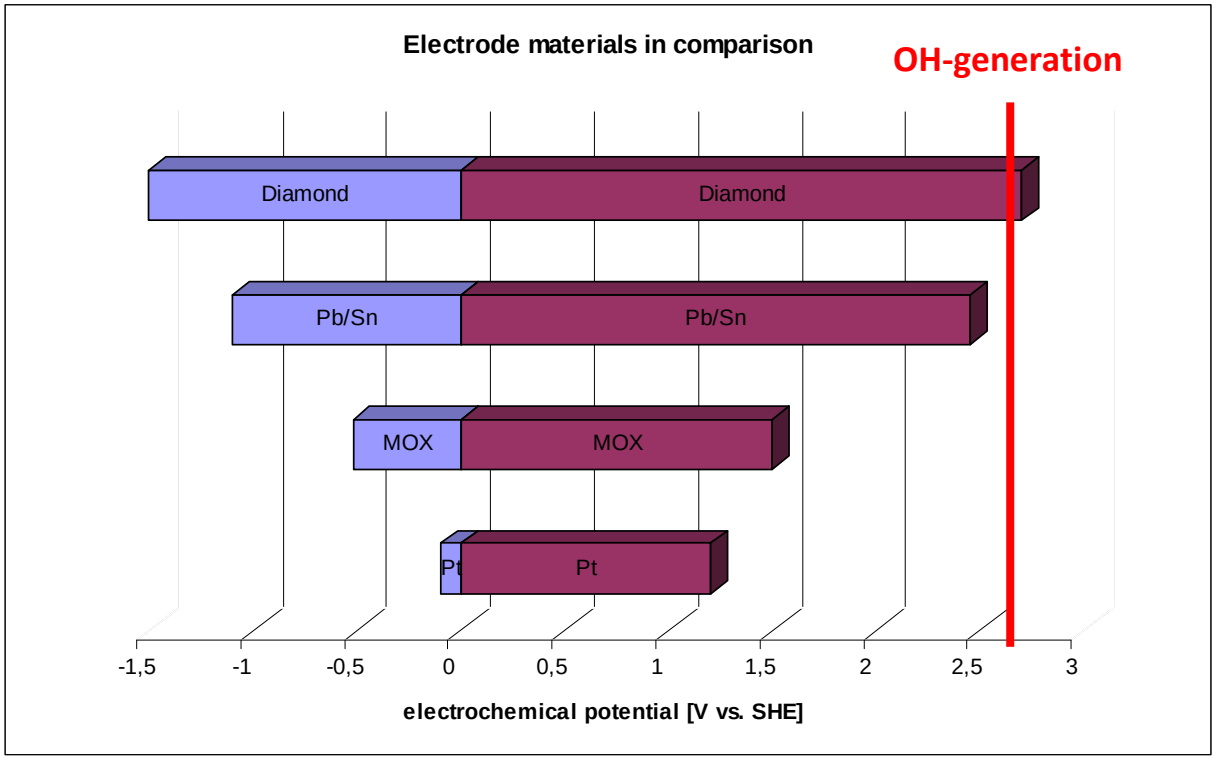




Source: Heidi B. Martin

Different electrode materials in comparison

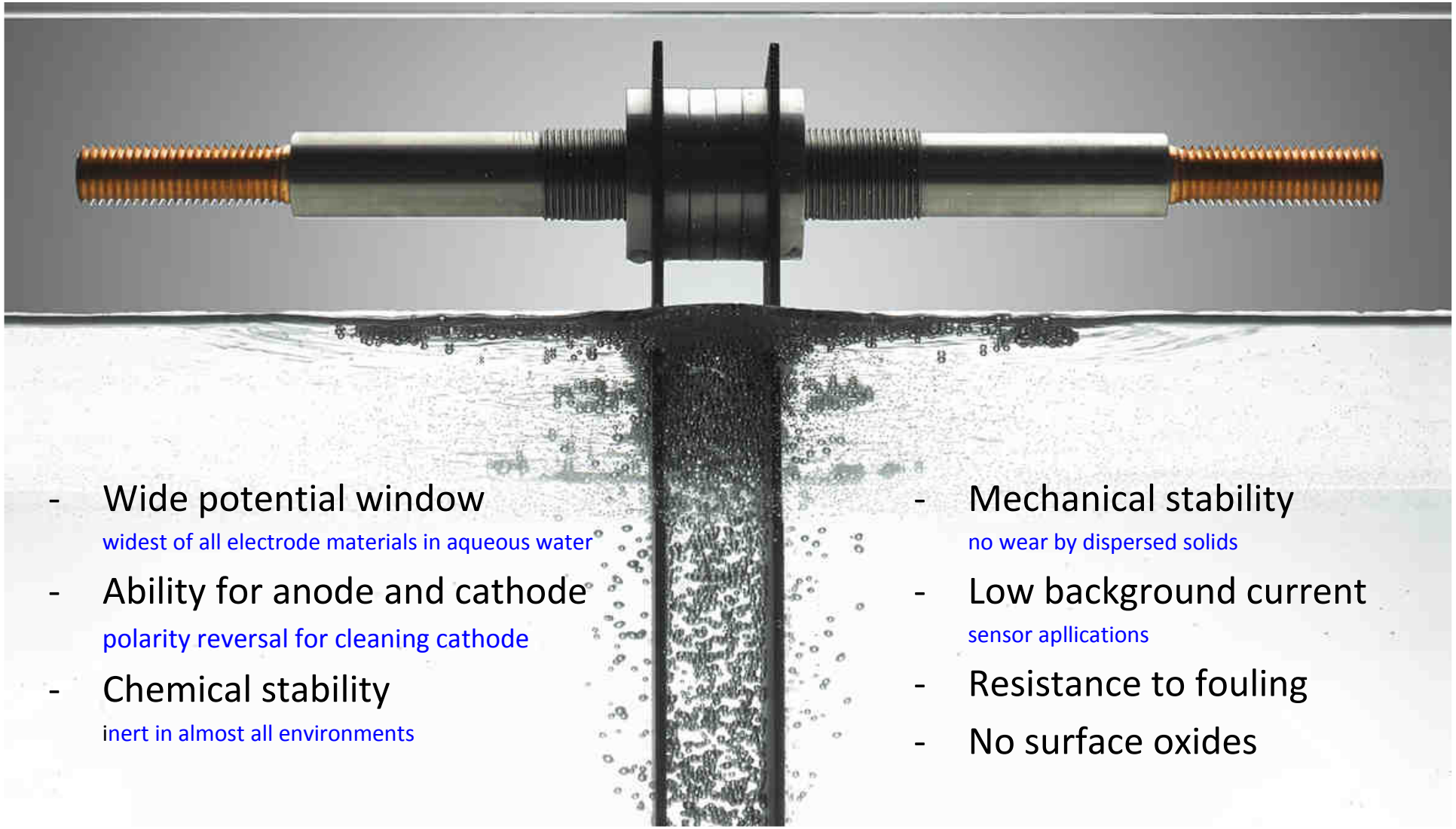
Diamond has the widest potential window for water decomposition



substance	formation potential [V]
Hydroxyl radical ($H_2O/OH^{\cdot}$)	2,80
Ozone (O_3)	2,07
Peroxodisulfate ($SO_4^{2-}/S_2O_8^{2-}$)	2,01
Hydrogen Peroxide (H_2O/H_2O_2)	1,77

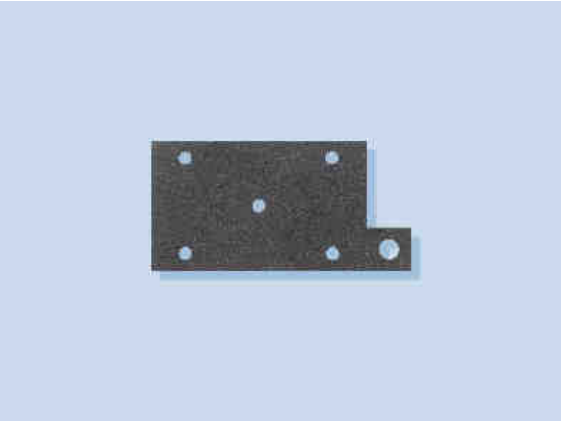
Source: Tröster

Properties of diamond electrodes at a glance



- Wide potential window
  widest of all electrode materials in aqueous water
- Ability for anode and cathode
  polarity reversal for cleaning cathode
- Chemical stability
  inert in almost all environments
- Mechanical stability
  no wear by dispersed solids
- Low background current
  sensor apllications
- Resistance to fouling
- No surface oxides

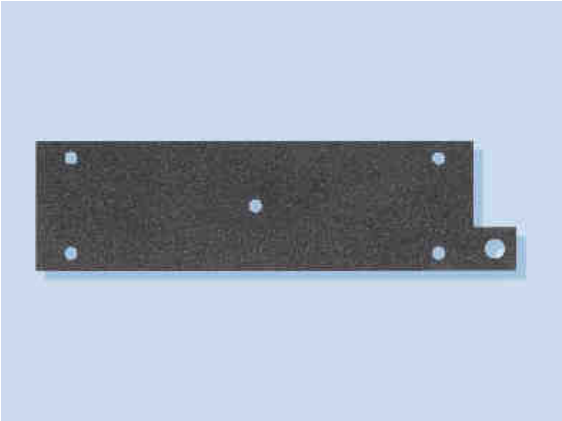
Equipment-Electrode types



Type Baerbel
250mmx150mm

Main types

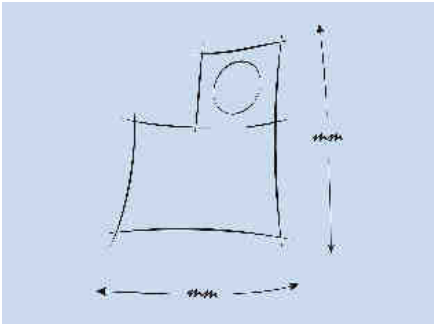
Standardised electrodes



Type Barbara
500mmx150mm

Mesh electrodes
welded connectors

Welded electrodes
large / complex geometries



Custom-made
water jet cut

Equipment-Electrolysers

Electrolysers for standard types

-Baerbel & Barbara Diamond electrodes

-0,075sqm - 0.95sqm anode/electrolyser

-ready made equipment

Equipment-Electrolysers

rd types

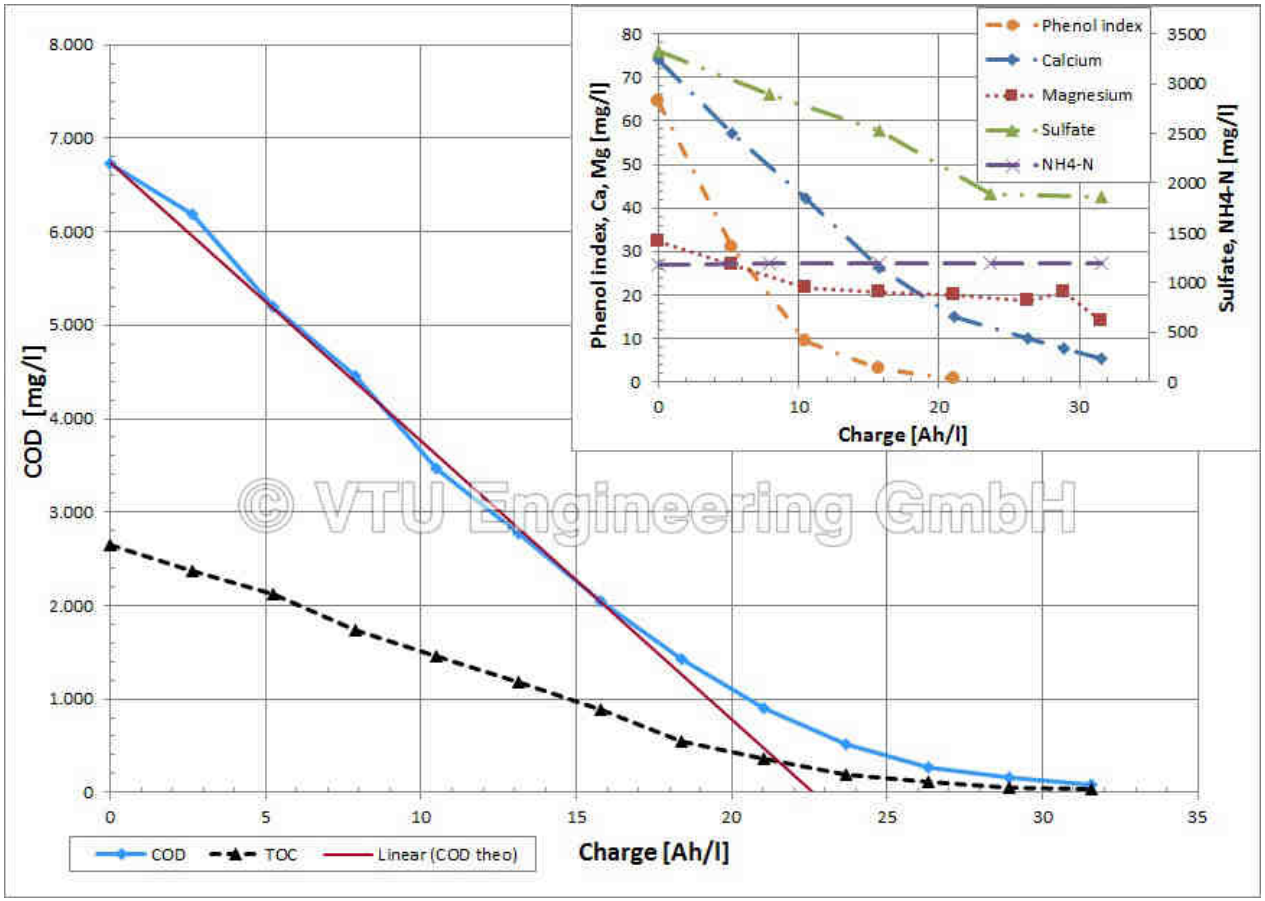
ctrodes

ctrolyser

-ready made equipment

Application - Treatment of phenol containing waste water

OH-radical is an extremely strong oxidant -> Oxidation of the waste



-Reduction of the **C**hemical **O**xygen **D**emand
(equivalent for contained waste)

-**A**dvanced **O**xidation **P**rocess

-No additional chemical re-
quired

Source:

Application- Treatment of waste water containing phenol

Powerful plants for treating different kinds of waste water

Baerbel-type

Barbara-type

Source:

Applications

Oxidation of an anticorrosive in a passivation bath

Original → Filtration → Oxidation with diamond electrodes

- **Standard procedure:** disposal — **190 EUR/m³**
- **New procedure:** Oxidation with Diamond electrodes & filtration — **45 EUR/m³**

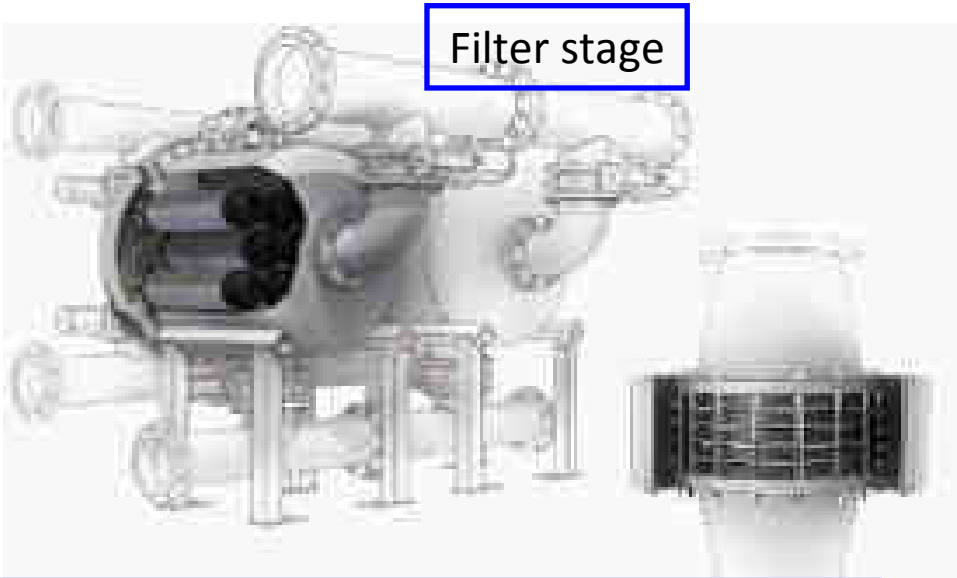
Oxidation of condensor water of a vaporizer

COD-reduction from 3000mg/L to 1000mg/L

- **Standard procedure:** disposal — **60 EUR/m³**
- **New procedure:** Adaption of pH-value & Oxidation with-Diamond electrodes — **14 EUR/m³**

Source: Coulomb Water

Application - Ballast water treatment

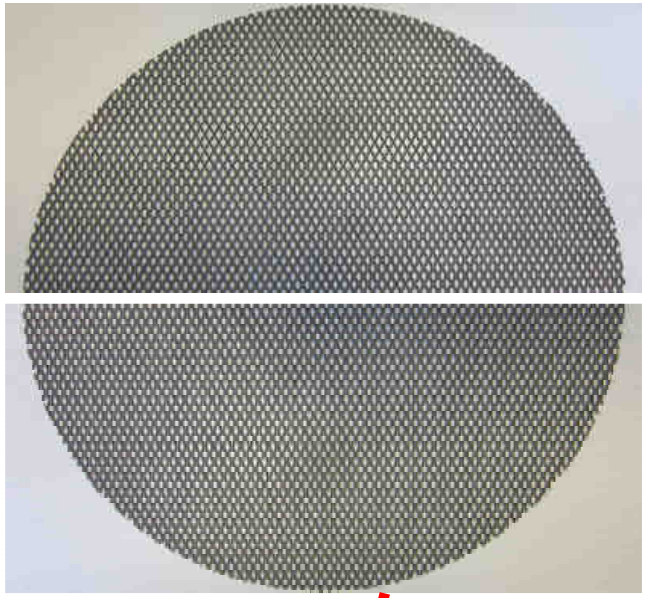


-Ballast water is required to stabilize ships in the sea

-transferred species can be-come a non control able invasion

-disinfection is required

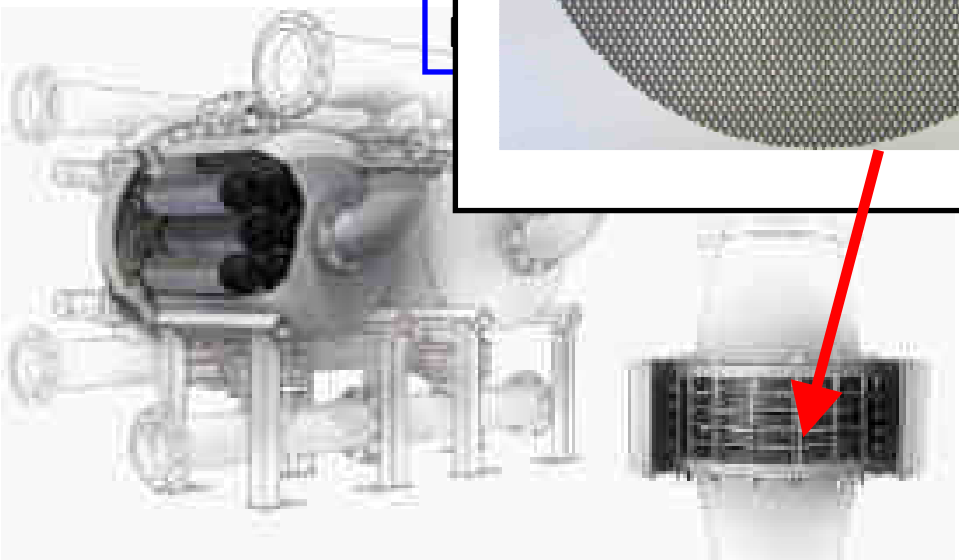
Application - Ball



Electrode-type:

-disc of two halves

-mesh type



Disinfection stage with diamond electrodes

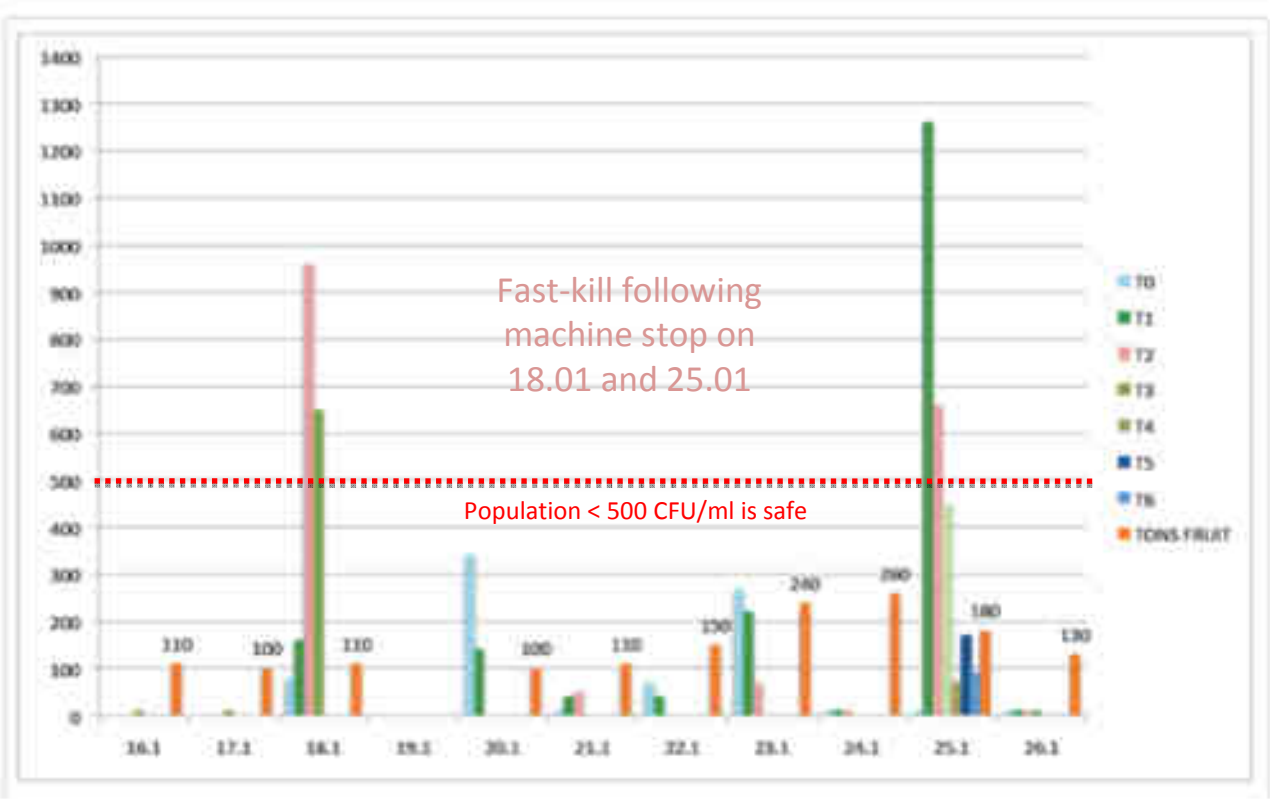
-transferred species can be-
come a non control able invasion

-disinfection is required

Rotten fruit by fungi **Penicillium spp.**

Application - disinfection in food processing

Conventional: Fruits are washed and treated with fungicides, high water consumption
With diamond electrodes: washing water is kept disinfected and no fungizides are required



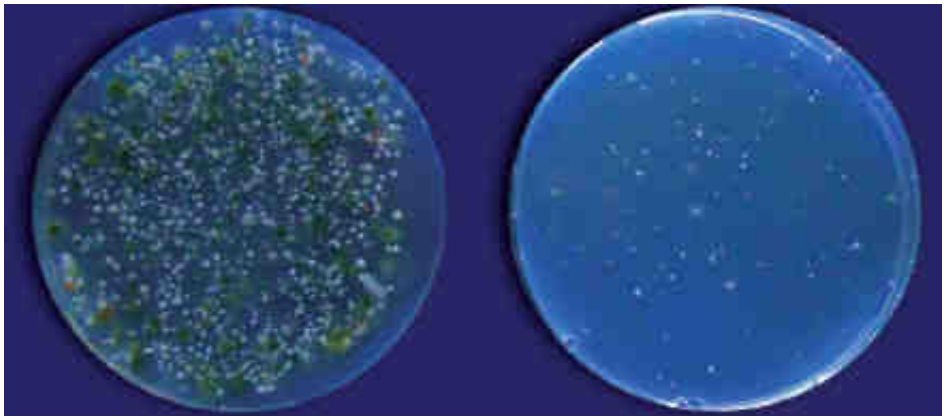
Population of Penicillium spp. (CFU – Colony Forming Units/ml) in citrus dip tank at Ortofrutticola Toro&Catena from 16 to 26 January 2014 – over 2800 tons of fruits have been processed

©AQANAT Limited

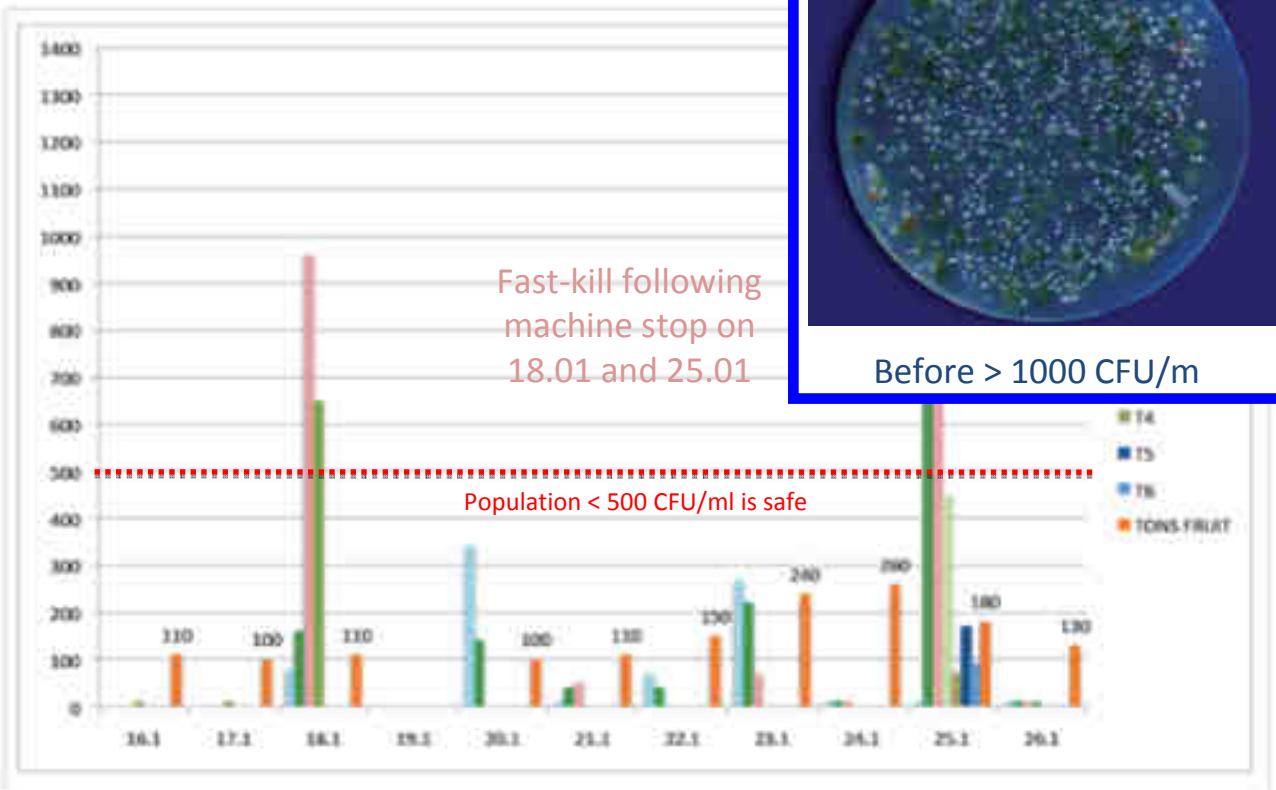
Application - disinfection in food processing

Conventional: Fruits are washed and treated
With diamond electrodes: washing water is k

typical view of grown and counted colonies



Before > 1000 CFU/m After 0-50 CFU/ml



Population of Penicillium spp. (CFU – Colony Forming Units/ml) in citrus dip tank at Ortofrutticola Toro&Catena from 16 to 26 January 2014 – over 2800 tons of fruits have been processed

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Application - Synthesis

Production of strong oxidizing substances

Substance	
ozone	2,07
Cerium (IV)	1,71
Peroxodisulfate	2,12
Silver (II)	1,98
ferrate	2,20
peroxycarbonate	1,80
periodate	1,60
peroxodiphosphate	2,07
permanganate	1,51

Source: A. Kraft

Advantages:

-Higher current efficiencies compared to conventional electrodes

-Replacement of precious metal electrodes

-Simplified processes

Application - Synthesis

Production of strong oxidizing substances

Substance	
ozone	2,07
Cerium (IV)	
Peroxodisulfate	
Silver (II)	
ferrate	
peroxycarbonate	
periodate	
peroxodiphosphate	2,07
permanganate	1,51

Source: A. Kraft

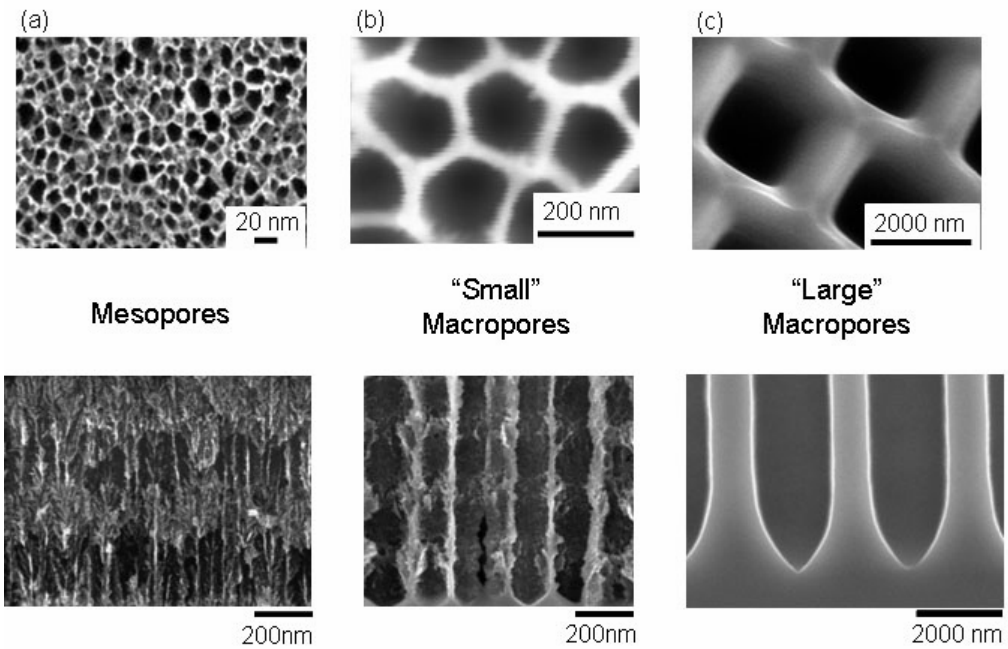
Advantages:

Electrode type:

-tube
-80mm & 170mm diameter
-520mm long

Application- Diamond electrodes as inert electrodes in porous Silicon production

Porous silicon is used in semiconductor industry, for sensors, filters and optical elements



Examples of porous Silicon

Source: ADVANCED MICROMACHINING TOOLS A.M.M.T

Application - Diamond electrodes as inert electrodes in porous Silicon production

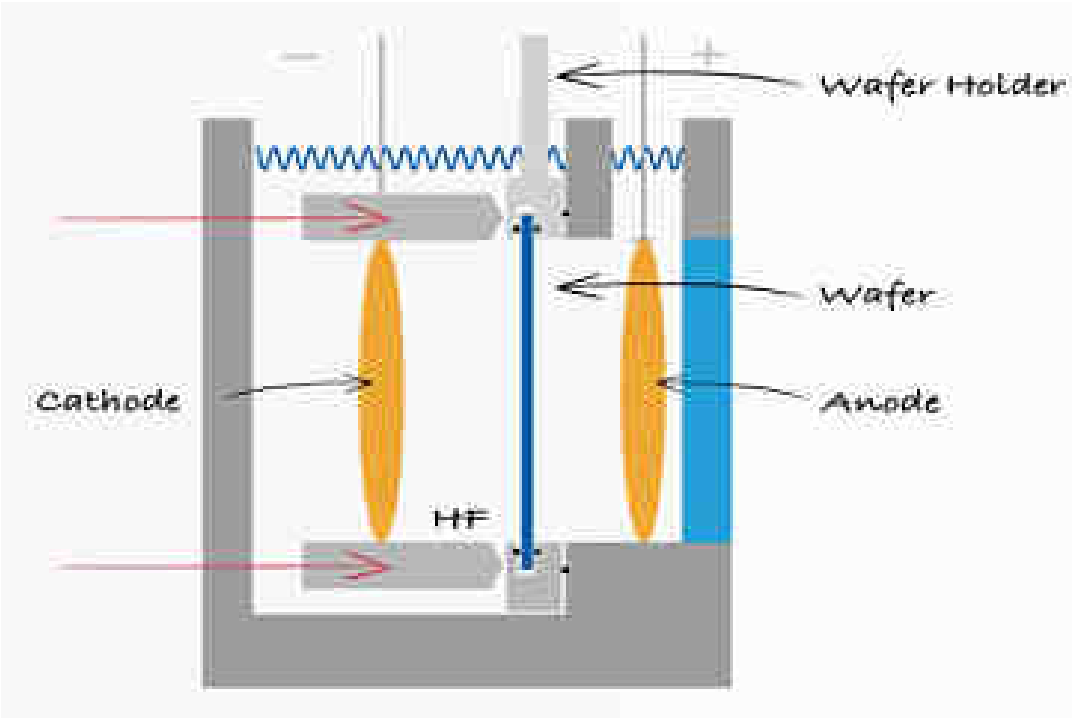
Microporous silicon is fabricated by etching silicon in Hydrofluoric acid-based solutions under applied voltage.

- **Platinum mesh**
  - Current limited

- **Platinum disk**
- *- expensive (Pt cost)*
  + High currents possible

- **Silicon Sacrificial**
  - consumed at etch-rate
  + metal free systems

- **Conductive diamond**
  + metal free / no consumption



Source: ADVANCED MICROMACHINING TOOLS A.M.M.T

Application - Diamond electrodes as inert electrodes in porous Silicon production

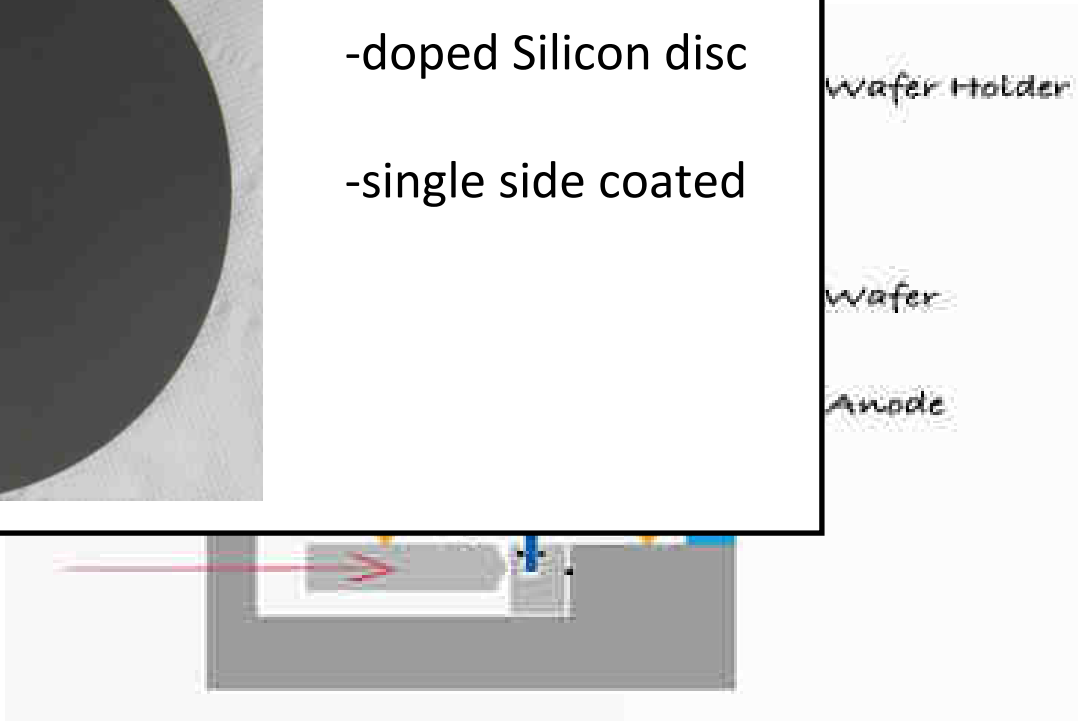
Microporou -based solutions u

- **Platinum**
  - Current
- **Platinum**
- *- expensi*
  + High cu
- **Silicon Sa**
  - consum
  + metal f
- **Conductive diamond**
  + metal free / no consumption

Electrode-type:

-doped Silicon disc

-single side coated



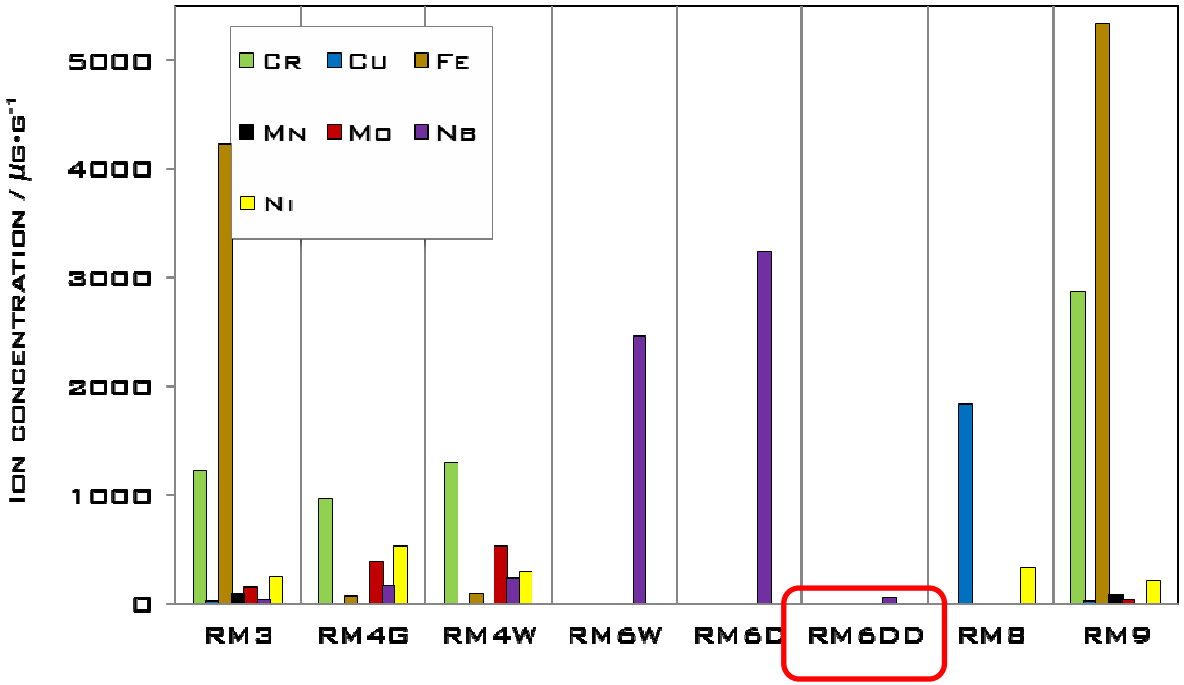
Source: ADVANCED MICROMACHINING TOOLS A.M.M.T

Gefördert durch:
Bundesministerium für Wirtschaft und Energie
aufgrund eines Beschlusses des Deutschen Bundestages

Application - Fuelcell (HTPEM)

Goal: Replacement of graphitic electrode for a metallic
Chemical resistance of BDD in screening test for fuel cells

Metal-ion concentration in concentrated phosphoric acid after corrosion test for 4 days at 160℃



sample	material
RM3	Cr-Ni-Mo-Austenite
RM4G	Ni-Cr-Mo-Nb-Austenite
RM4W	Ni-Cr-Mo-Nb-Austenite
RM6W	Nb
RM6D	Nb
RM6DD	Diamond coating on Nb
RM8	CuNi25
RM9	Ni-Cr-Austenite

Source: Forschungzentrum Jülich, Institut für Energie- und Klimaforschung IEK-3

Application - Fuelcell (HTPEM)

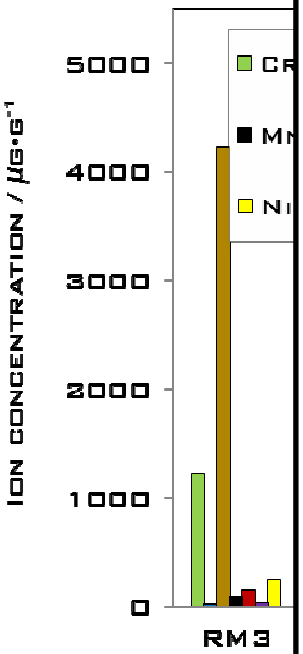
Gefördert durch:

Bundesministerium für Wirtschaft und Energie

aufgrund eines Beschlusses des Deutschen Bundestages

Goal: Repla
Chemical re

Metal-ion co
acid after co

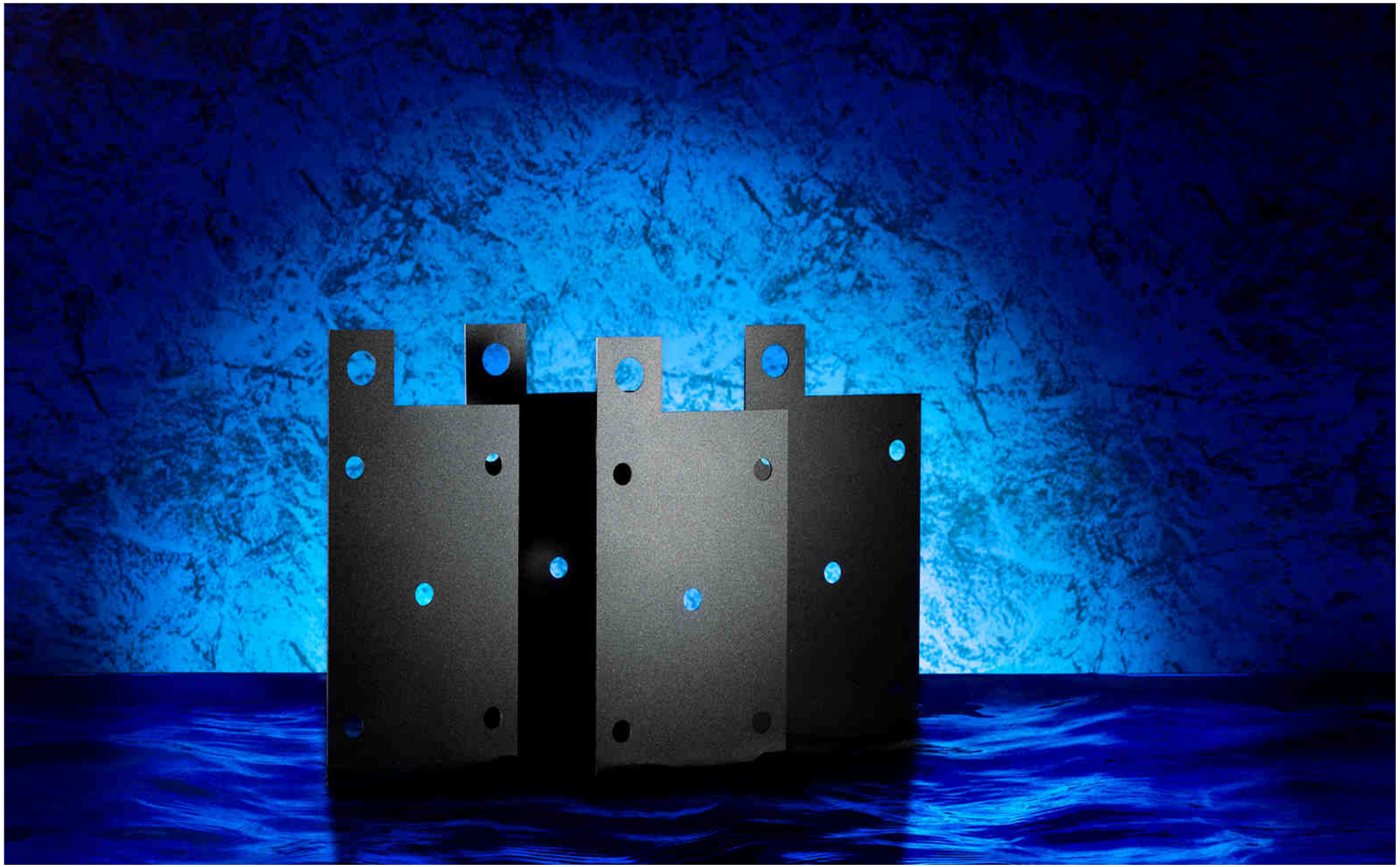


Prototype:

HTPEM – fuell cell with diamond electrodes

aterial
lo-Austenite
-Nb-Austenite
-Nb-Austenite
Nb
Nb
coating on Nb
uNi25
-Austenite

Source: Forschungzentrum Jülich, Institut für Energie- und Klimaforschung IEK-3



Thank you!