Electroplated Tin-Nickel Coatings as a Replacement for Nickel to Eliminate Nickel Dermatitis

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Introduction:

Professor **Corrosion & Surface Technology**
The Technical University of Denmark

Initiator and manager of several research projects: *electro-catalytic-materials for hydrogen production, catalytic material for methanization, antibacterial surfaces electro-catalytic and photo-catalytic, low friction coating for combustion engines, nickel dermatitis/replacement, corrosion of medical implants in vivo and in vitro etc.*

130 scientific articles and 25 patents

Book: Advanced surface Technology *"A holisic view on the extensive and intertwined world of applied surface engineering"* by Per Møller & Lars Pleth Nielsen

1200 pages

Nickel dermatitis (skin allergy) is a growing problem in numerous countries. The alarming frequency of sensitization to nickel especially in the US caused nickel to be selected as the ***"Allergen of the Year"*** *in 2008 by* ***the American Contact Dermatitis Society****. Nickel as coating in contact with skin has already been regulated by the nickel* ***EU directive [94/27/EC] since 1994****. In the present contribution tin/nickel alloy coatings (66.9 wt. % Sn), electrodeposited from a chloride/fluoride containing alloy electrolyte, will be presented as an alternative for both nickel and bright chromium coatings.*

American Contact Dermatitis Society

Promoting Excellence in Contact Dermatitis & Occupational Dermatology Research, Practice & Education

Nickel dermatitis

Nickel dermatitis

Press focuses on nickel dermatitis

Nickel allergy is one of the most common causes of allergic contact dermatitis — an itchy rash that appears when your skin touches a usually harmless substance.
Nickel allergy can affect people of all ages. A nickel allergy usually develops after repeated or prolonged exposure to items containing nickel. Treatments can reduce the symptoms of nickel allergy. Once you develop nickel allergy, however, you will always be sensitive to the metal and should avoid contact.

Cited CNN

Nickel may be released from laptop computers

Peter Jensen[1], Morten S. Jellesen[2], Per Møller[2], Jeanne D. Johansen[3], Carola Lidén[4], Torkil Menné[1] and Jacob P. Thyssen[3]

[1] Department of Dermato-Allergology, Copenhagen University Hospital Gentofte, DK-2900 Hellerup, Denmark, [2] Department of Mechanical Engineering, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark, [3] Department of Dermato-Allergology, National Allergy Research Centre, Copenhagen University Hospital Gentofte, DK-2900 Hellerup, Denmark and [4] Institute of Environmental Medicine, Karolinska Institutet, SE-171 77 Stockholm, Sweden

doi:10.1111/j.1600-0536.2012.02162.x

Key words: consumer; dermatitis; nickel.

computers, we investigated a random sample of 20

each solution in succession on a white cotton wool-tipp
applicator, which was rubbed for up to 20 seconds aga
the test object. A positive reaction was indicated by
coloration of the applicator, and a negative reacti
registered when no colour change was observ
doubtful reactions, defined as very weak pink
or discoloration possibly masking a pink colou
rformed, and if the reaction remained
to be doubtful. We tested
ttom surfaces of
ts (bot

Content

The history and the interest of Tin/Nickel

The Tin/Nickel Alloy & The Tin/Nickel Process

Tin/Nickel and Nickel – allergic (contact dermatitis)?

Corrosion properties of Tin/Nickel

Tin/Nickel was first time described of Monk and Ellingham 1935

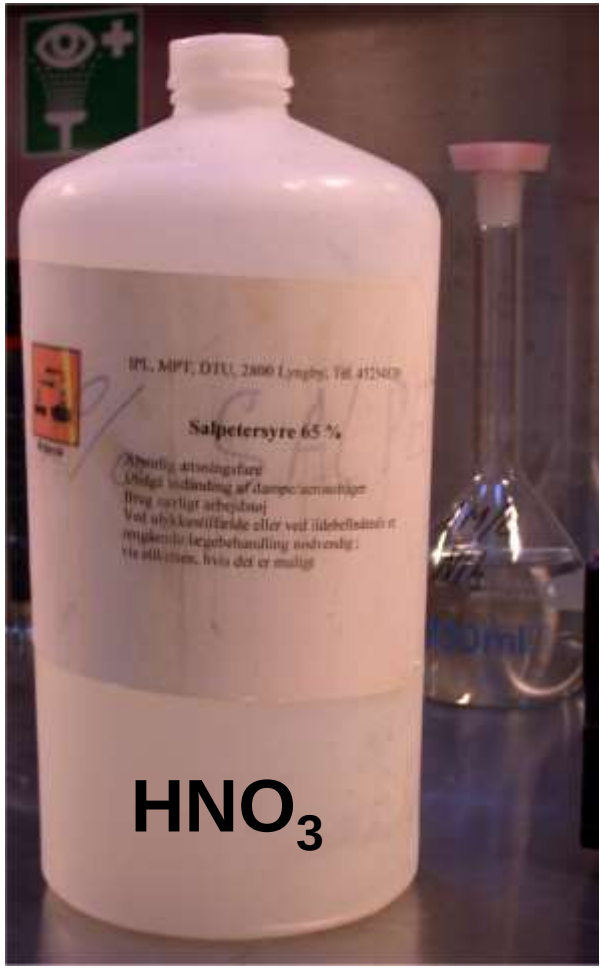
Later a proces was developed by
Tin Research Institute and published

N. Parkinson, *J. Electrodep.Tech. Soc*. 27, 129 (1951).

~~**Journal of Electrodepositors´ Technical Society.**~~

Institute of Metal Finishing Transactions

Tin/Nickel



Tin/Nickel coated braas immersed in Nitric acid

Tin/Nickel

Sn/Ni plated brass

Stainless steel pipe for draught beer

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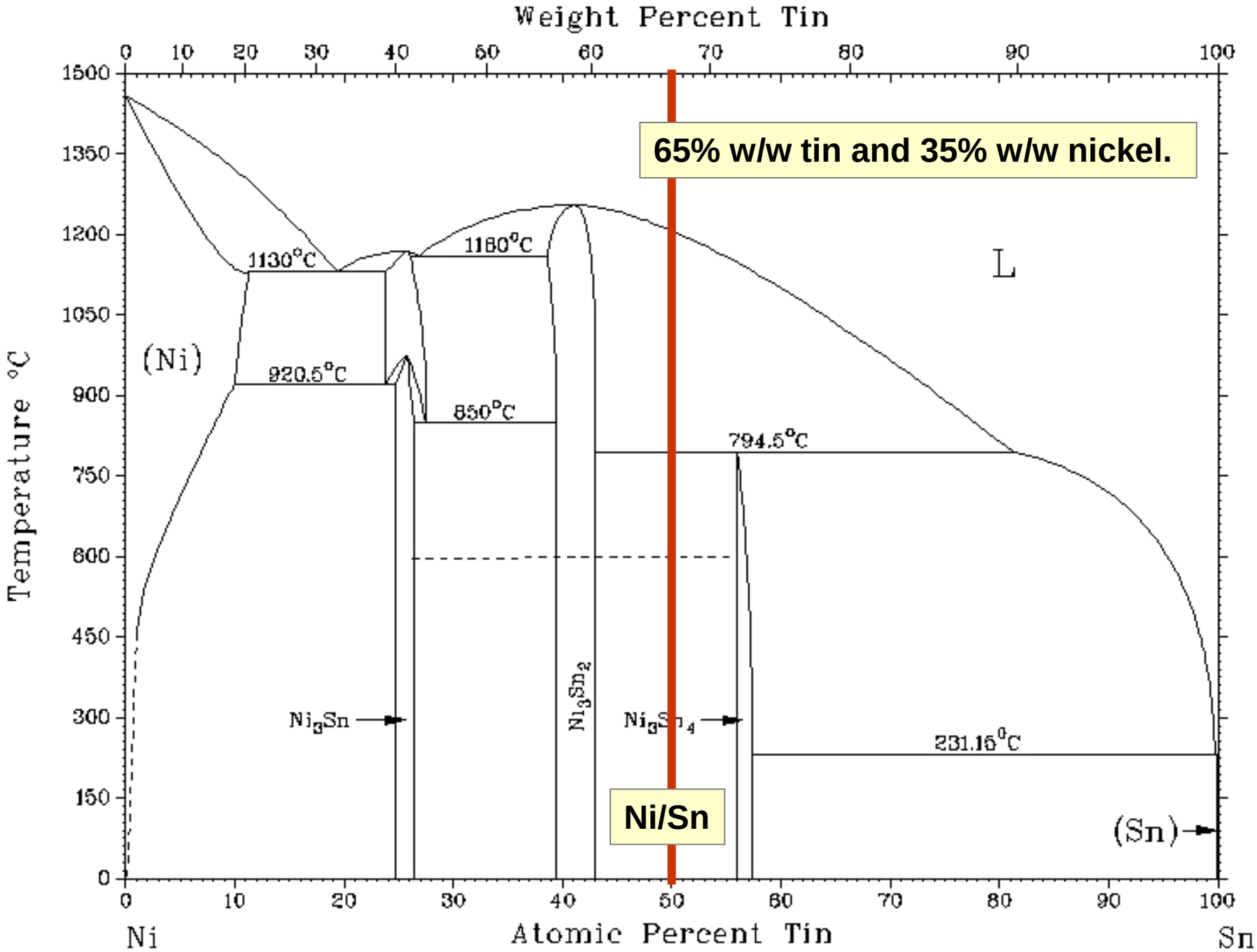
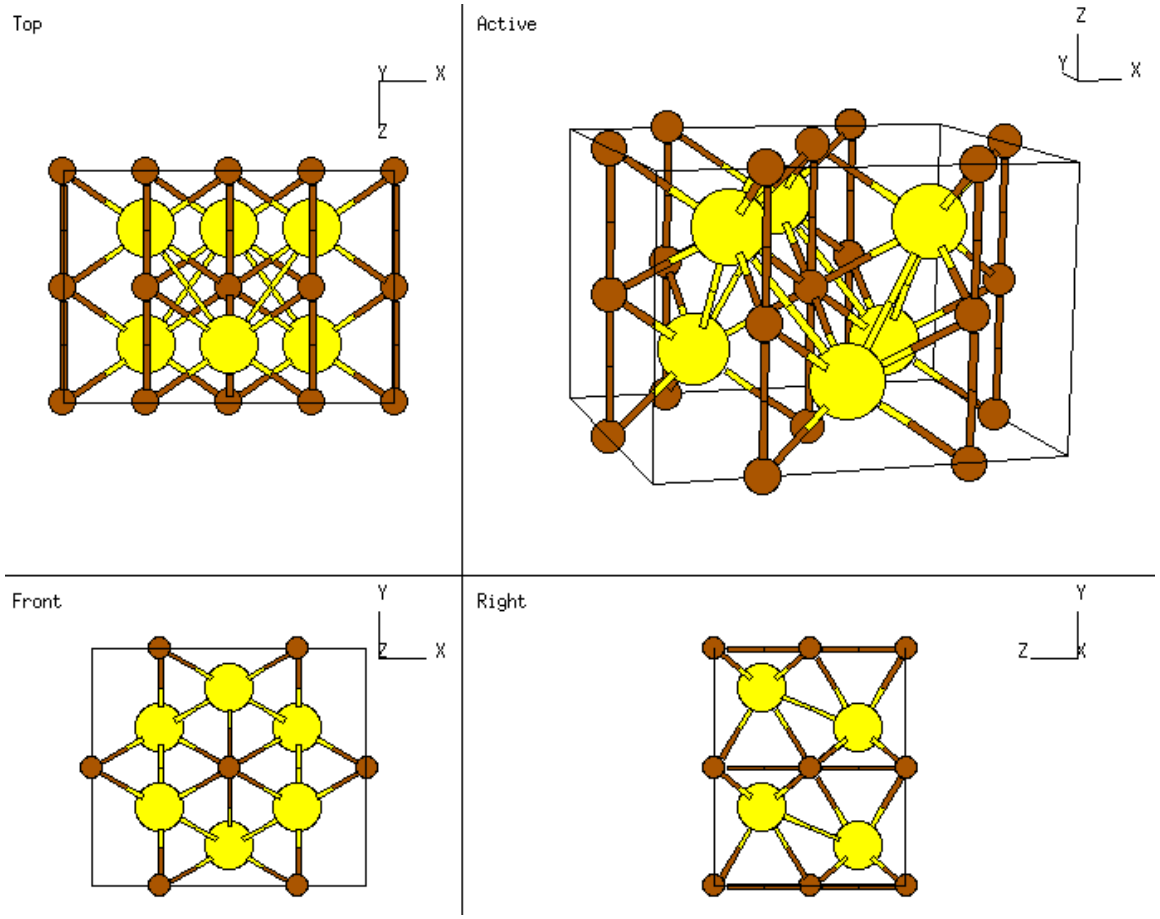

Weight Percent Tin
0 10 20 30 40 50 60 70 80 90 100
1500 1350 1200 1050 900 750 600 450 300 150 0
Temperature °C
65% w/w tin and 35% w/w nickel.
1130°C
1180°C
L
(Ni)
920.5°C
850°C
794.5°C
Ni3Sn
Ni3Sn2
Ni3Sn4
231.15°C
Ni/Sn
(Sn)
0 10 20 30 40 50 60 70 80 90 100
Ni
Atomic Percent Tin
Sn

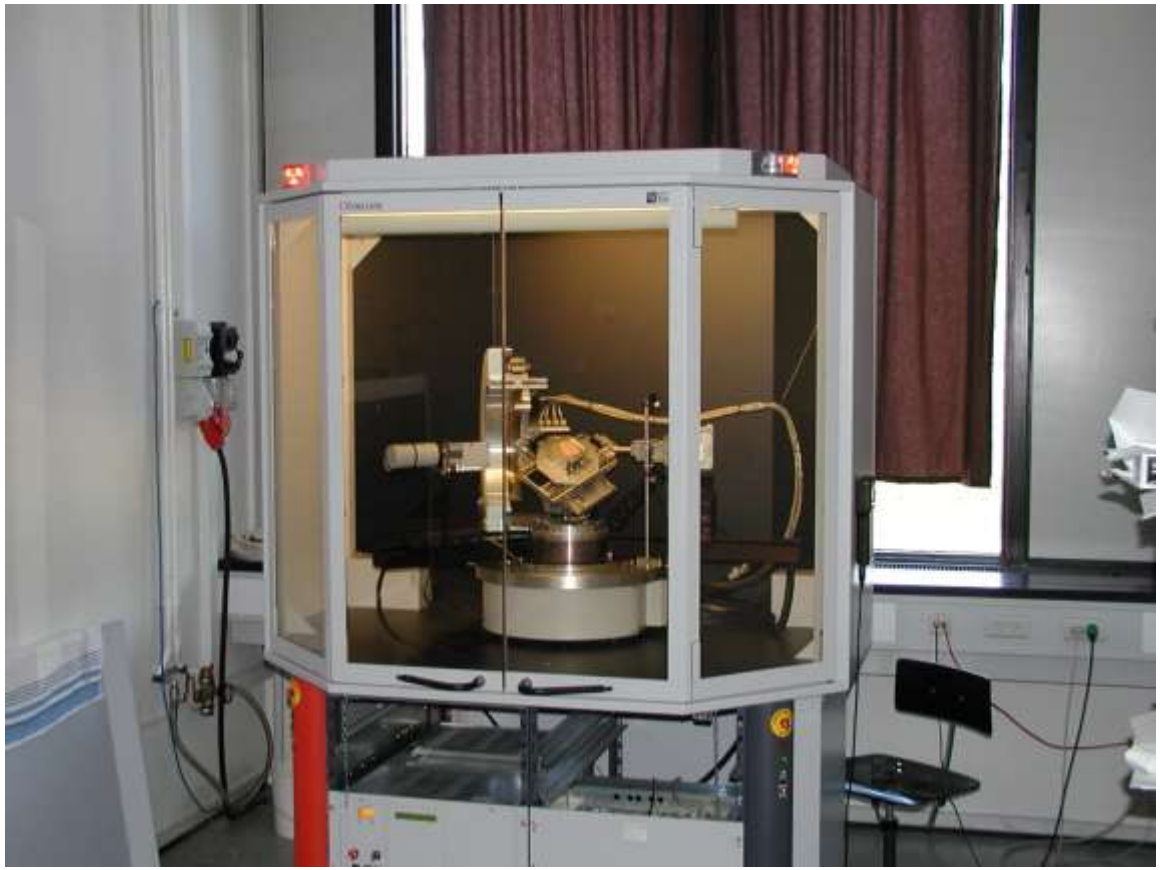
The crystal structure of the Electrodeposited Sn/Ni was early stated to have a hexagonal structure like Cu_6Sn_5 of the type NiAs ($B8_1$) Structure



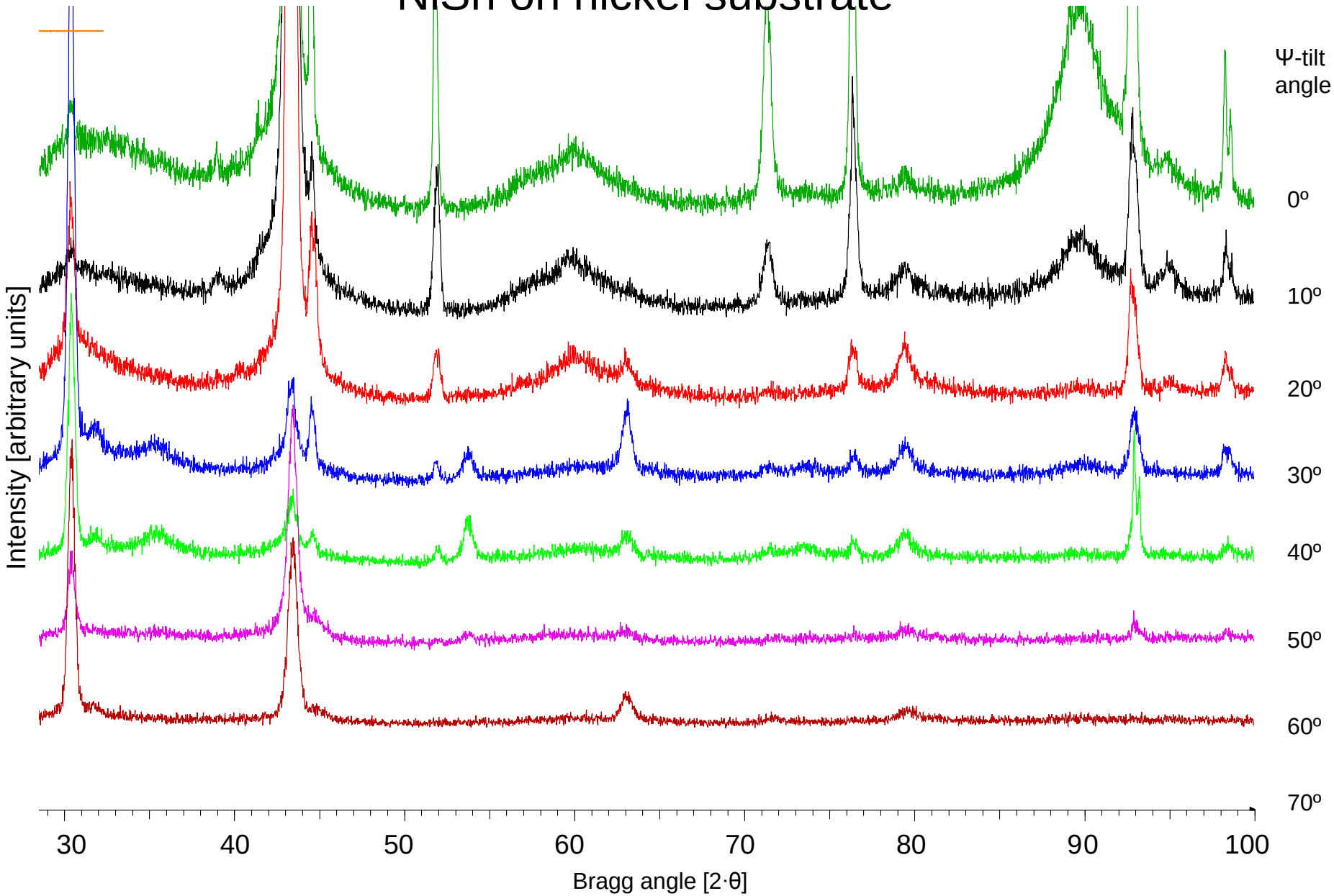
The process is based on an acid chloride/fluoride electrolyte which give the single phase intermetallic compound NiSn containing approximately 65% w/w tin and 35% w/w nickel.

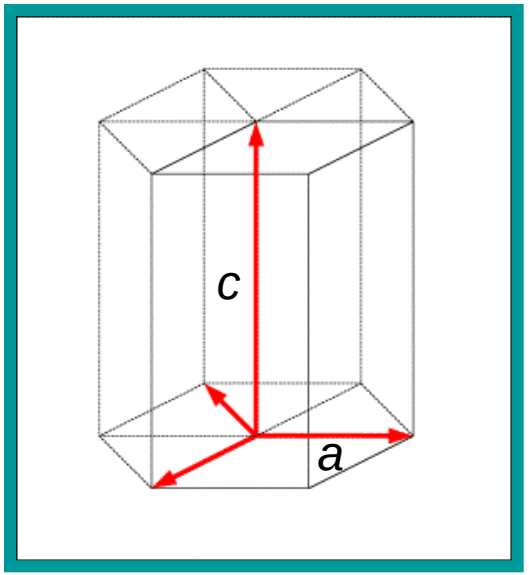
Ni 60-65 g/l
Sn 20-25 g/l
30 g/l Stabilizer
pH 4 - 4.6

X-ray diffraction patterns (CuK_α) of electrodeposited NiSn on nickel substrate



X-ray diffraction patterns (CuK_α) of electrodeposited NiSn on nickel substrate





c = 5.10 Å

a = 4.15 Å

c = 5.123 Å

a = 4.173 Å

Results from The Technical University of Denmark

C.C Lo, Structure of electrodeposited equiatomic tin-nickel alloy, *J. Appl. Phys.* 51(4) (1980).

Conclusion: A hexagonal structure like described earlier

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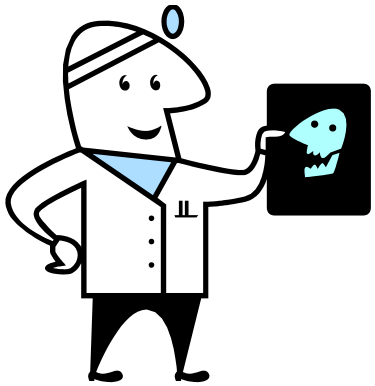


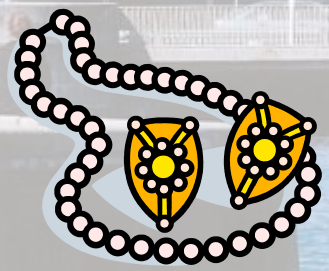
Danish Government in Copenhagen

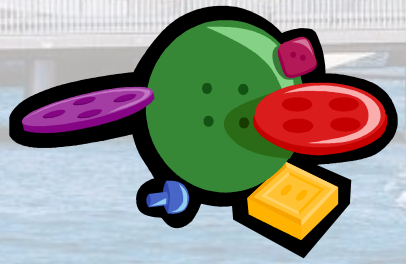
Danish law:

(BEK nr 854 af 16/12/1991)

22 years ago

Departmental order about embargo for sales of "special products" of nickel or nickel alloys, which could release more than **0,5 µg Ni/cm²/week**





zippers

Lidén T. Menné and D. Burrows: Nickel-containing alloys and platings and their ability to cause dermatitis. British Journal of Dermatology 1996; 134: 193-198

Nickel dermatitis from contact with jeans studs (left) and necklace (right)

Lidén T. Menné and D. Burrows: Nickel-containing alloys and platings and their ability to cause dermatitis. British Journal of Dermatology 1996; 134: 193-198

Nickel dermatitis from contact with nickel plated paint spray gun.

Patch tests on the back

The presence of a rash under an individual allergen indicates sensitivity to this substance. This does not prove that this particular allergen is the cause, but may provide a clue of what may be causing the problem.

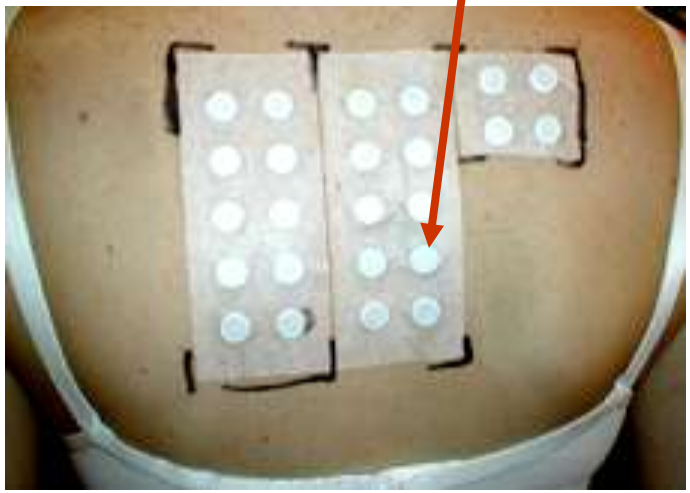
Nickel coated brass

Patch tests on the back

Stainless steel 316

Patch tests on the back

Tin plated brass ***control***



Patch tests on the back

Patch tests on the back

Patch test results.

The body's immune system recognizes allergen as "foreign". When this happens, white cells are attracted from the blood into the skin over several days. This results in inflammation and the development of a rash.

Artificial sweat 0,5% NaCl, 0,1% milk-acid and 0,1% urea. pH correction with ammonia to 6,5.

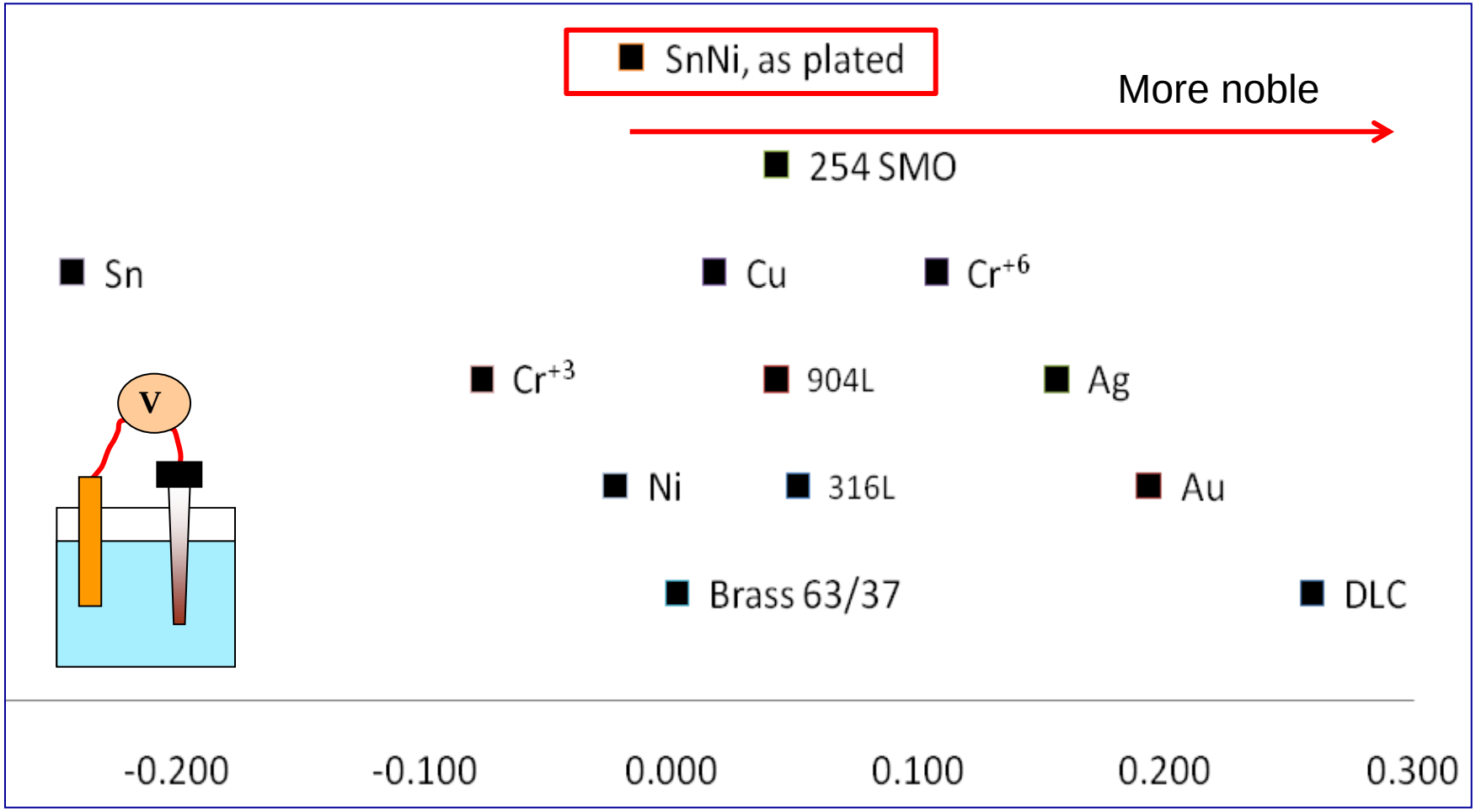
Critical release of Ni 0,5 μg/cm²/week

Metal	Nickel content in %	Release in microgram pr cm² pr week in the beginning	Release in microgram pr cm² pr week after 3 weeks.	Allergic skin reaction from persons with nickelallergy
Elektrolytic nickel	100	10	70	75
Nickel/Tin	35	0,5	0,1	22
Coin metal	25	6	3	(not measured)
Stainless Steel	9	0,04	0,01	3
White Gold	15	0,3	0,02	11
Tin coating on copper	0	0	0	10

Source: Miljøprojekt nr. 90 : “Nikkelafgivelse fra metallegeringer” Miljøstyrelsen 1988.

CONTENT

Corrosion potential of Tin/Nickel alloy compared with selected metals.



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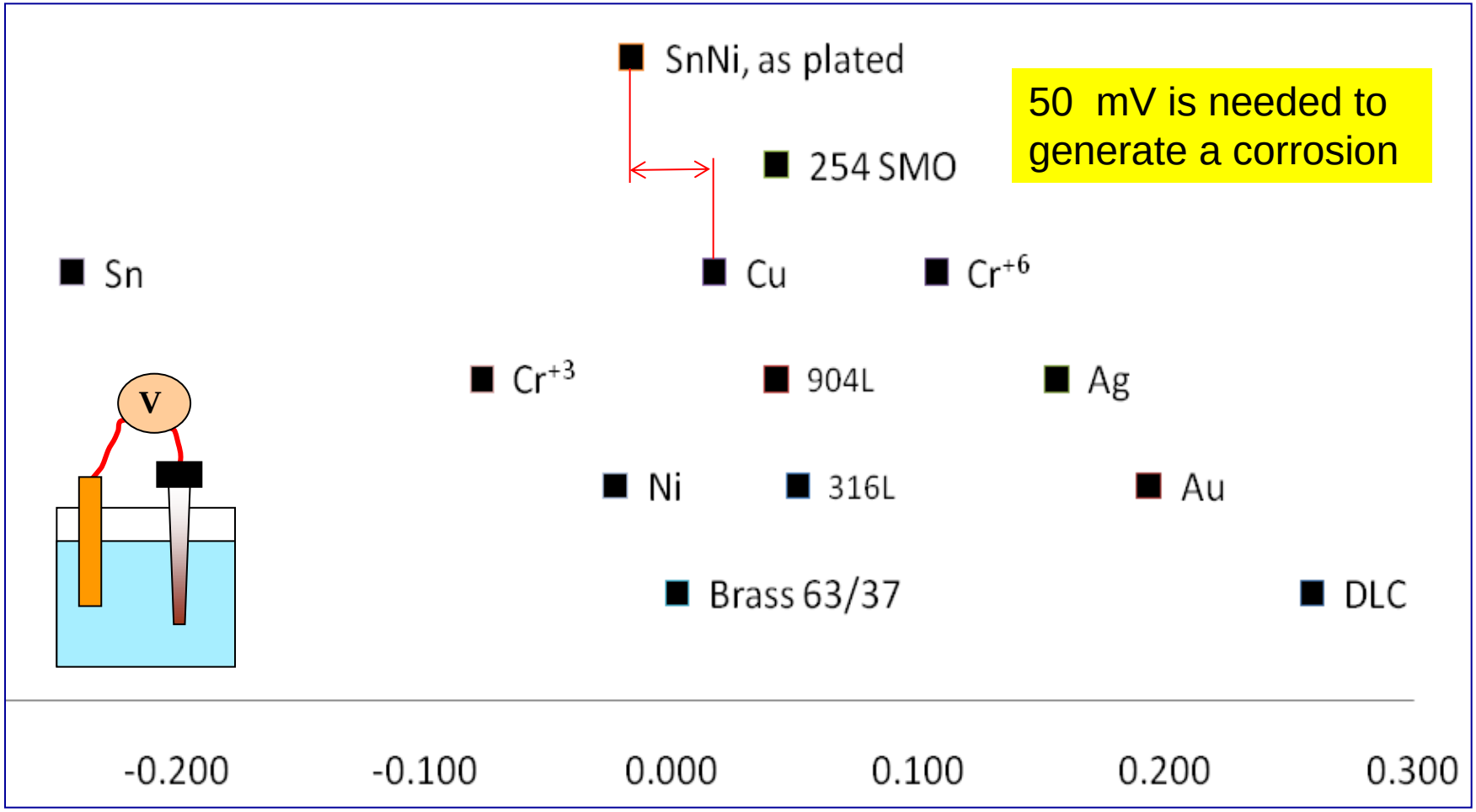

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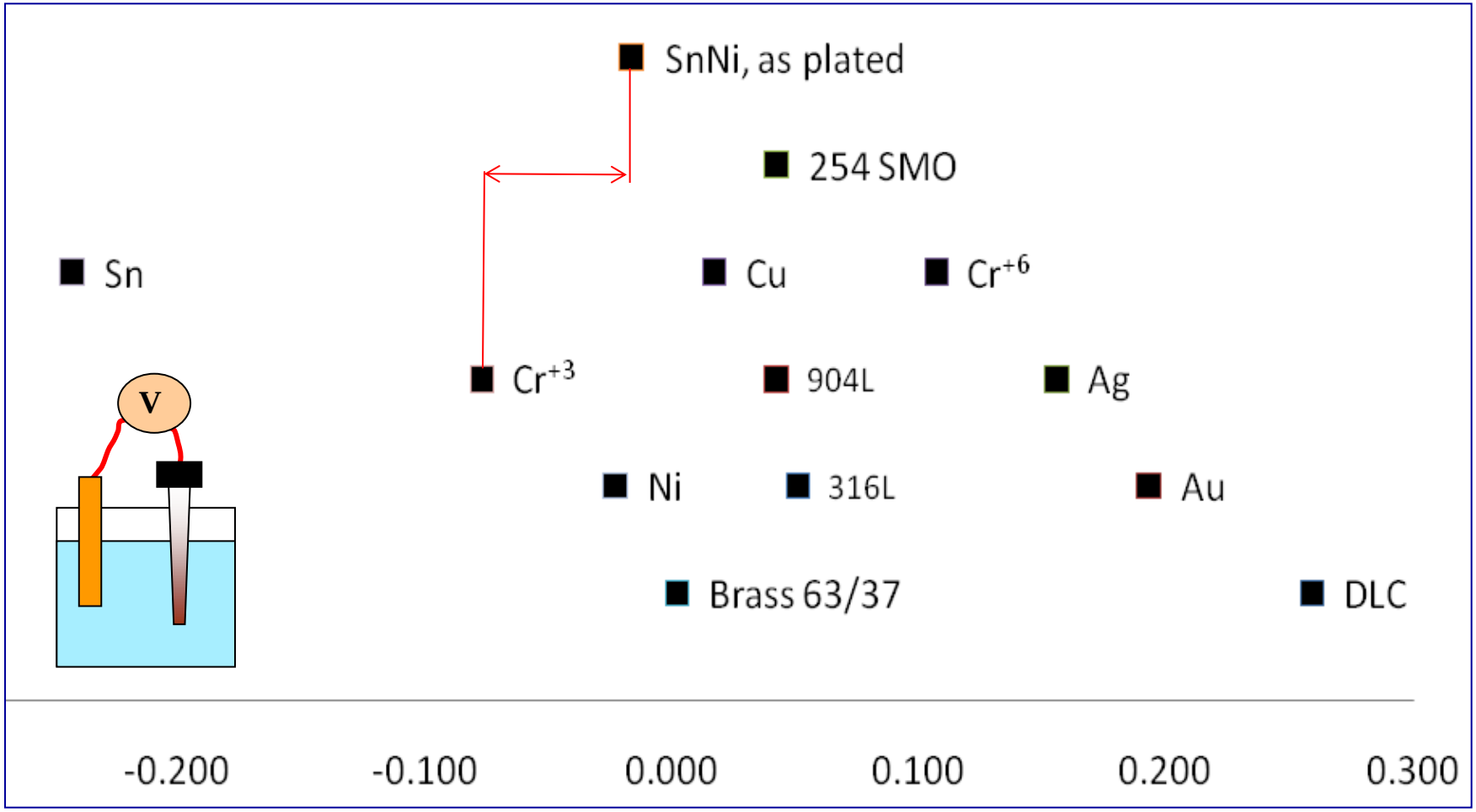
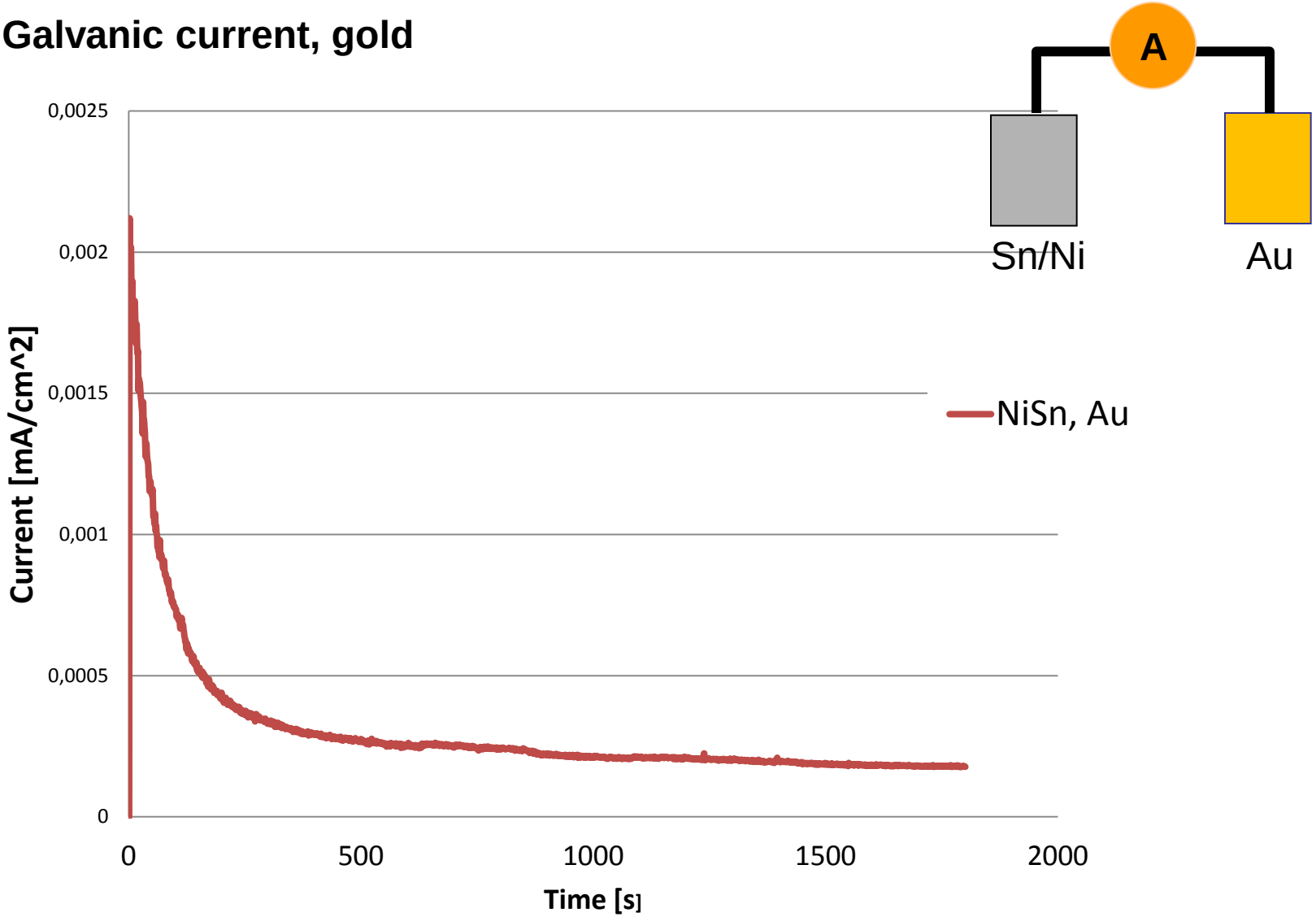
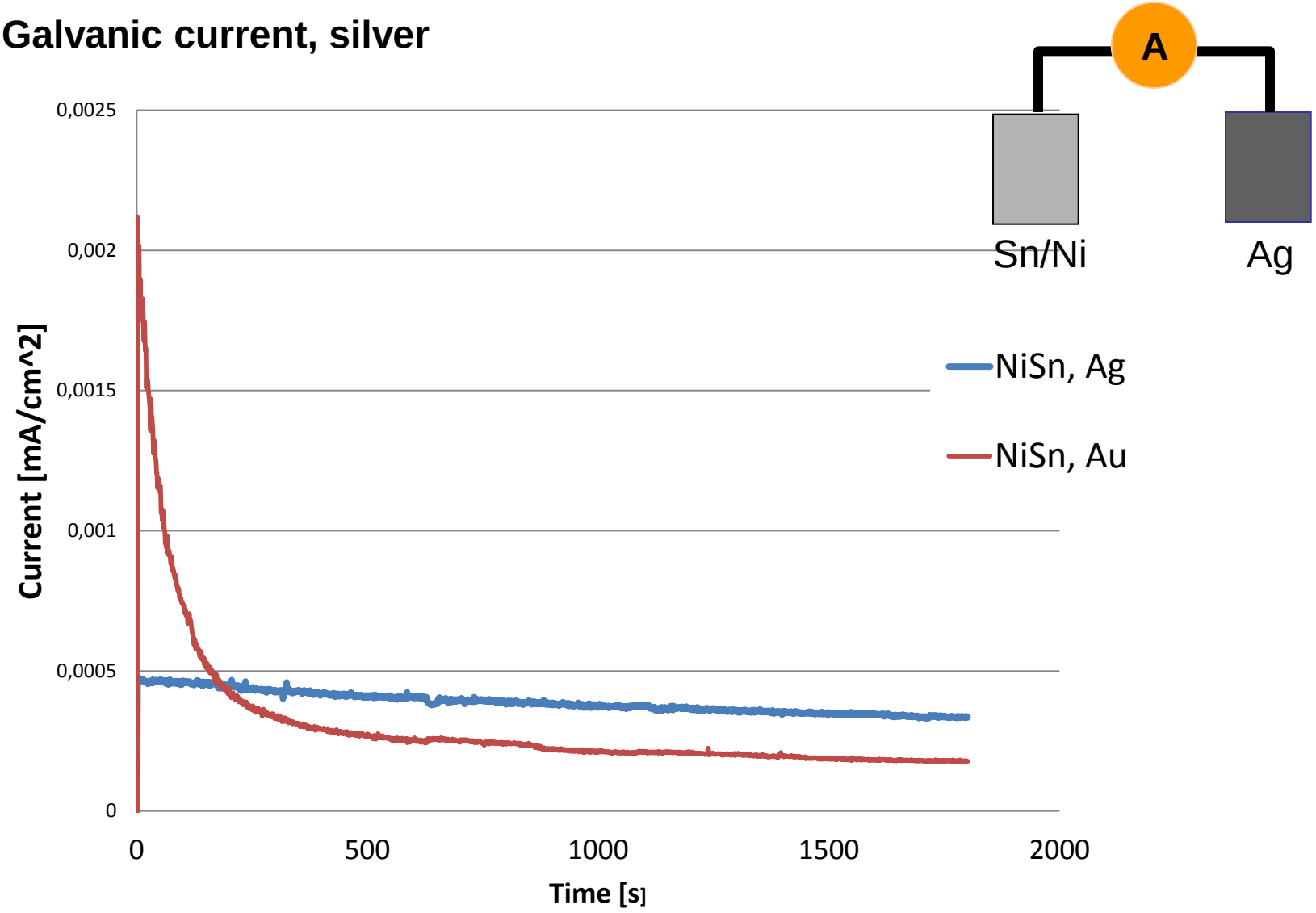


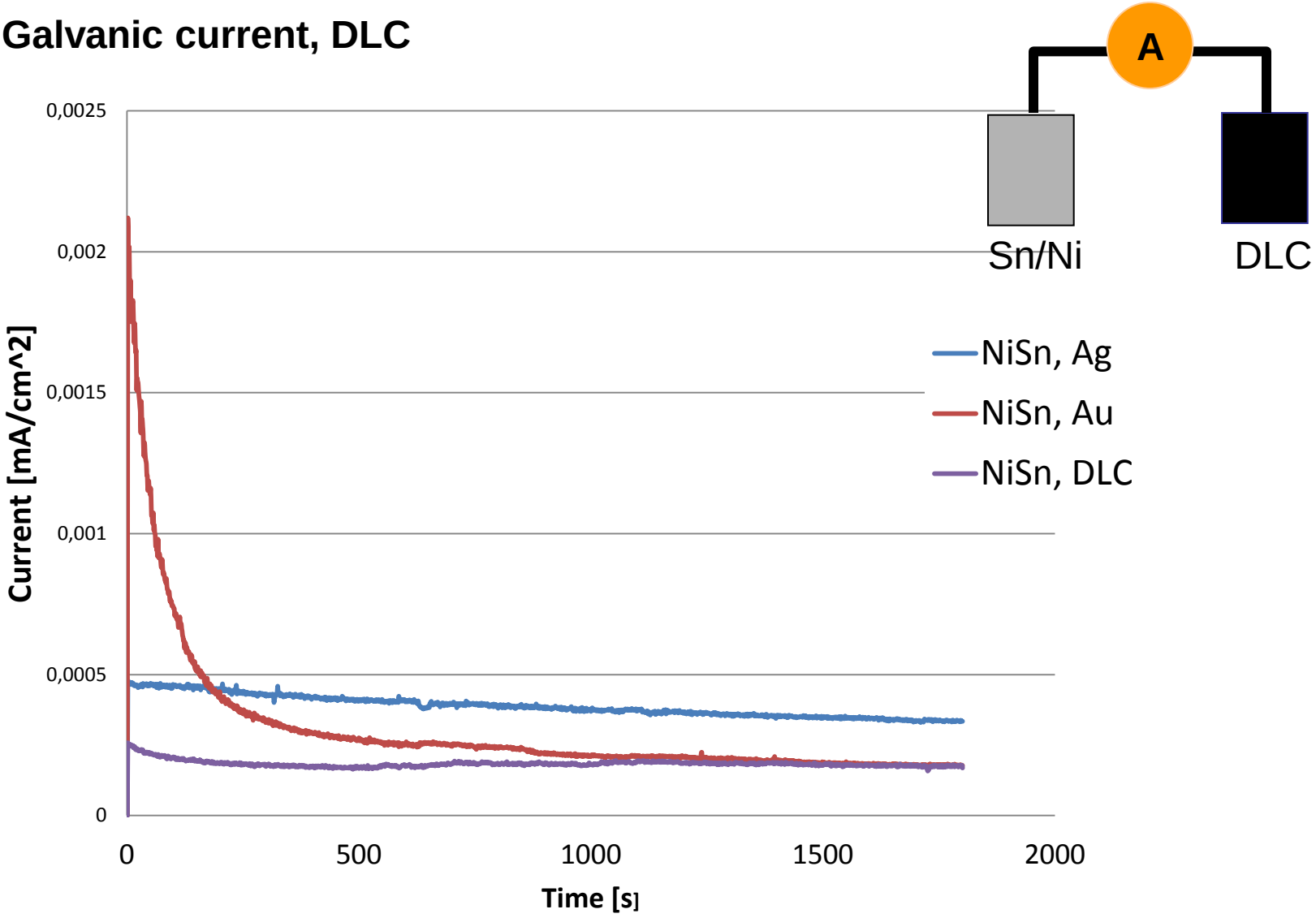
Galvanic current, gold



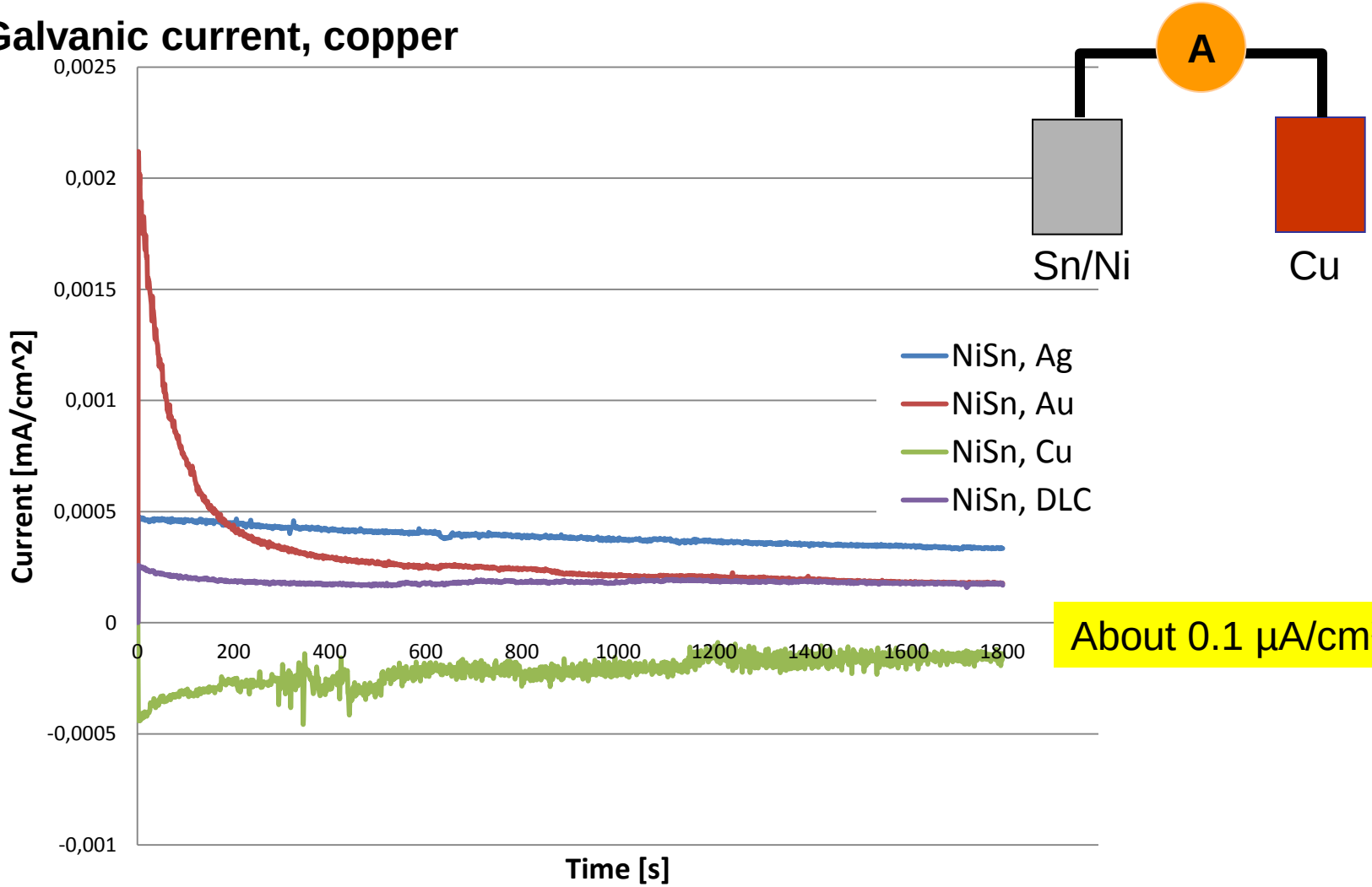
Galvanic current, silver



Galvanic current, DLC



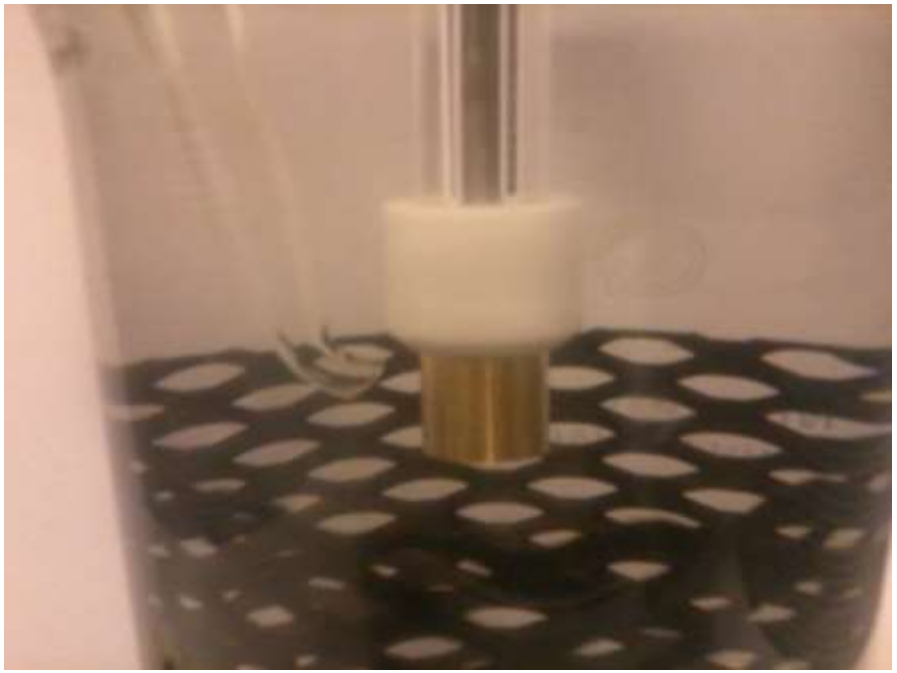
Galvanic current, copper



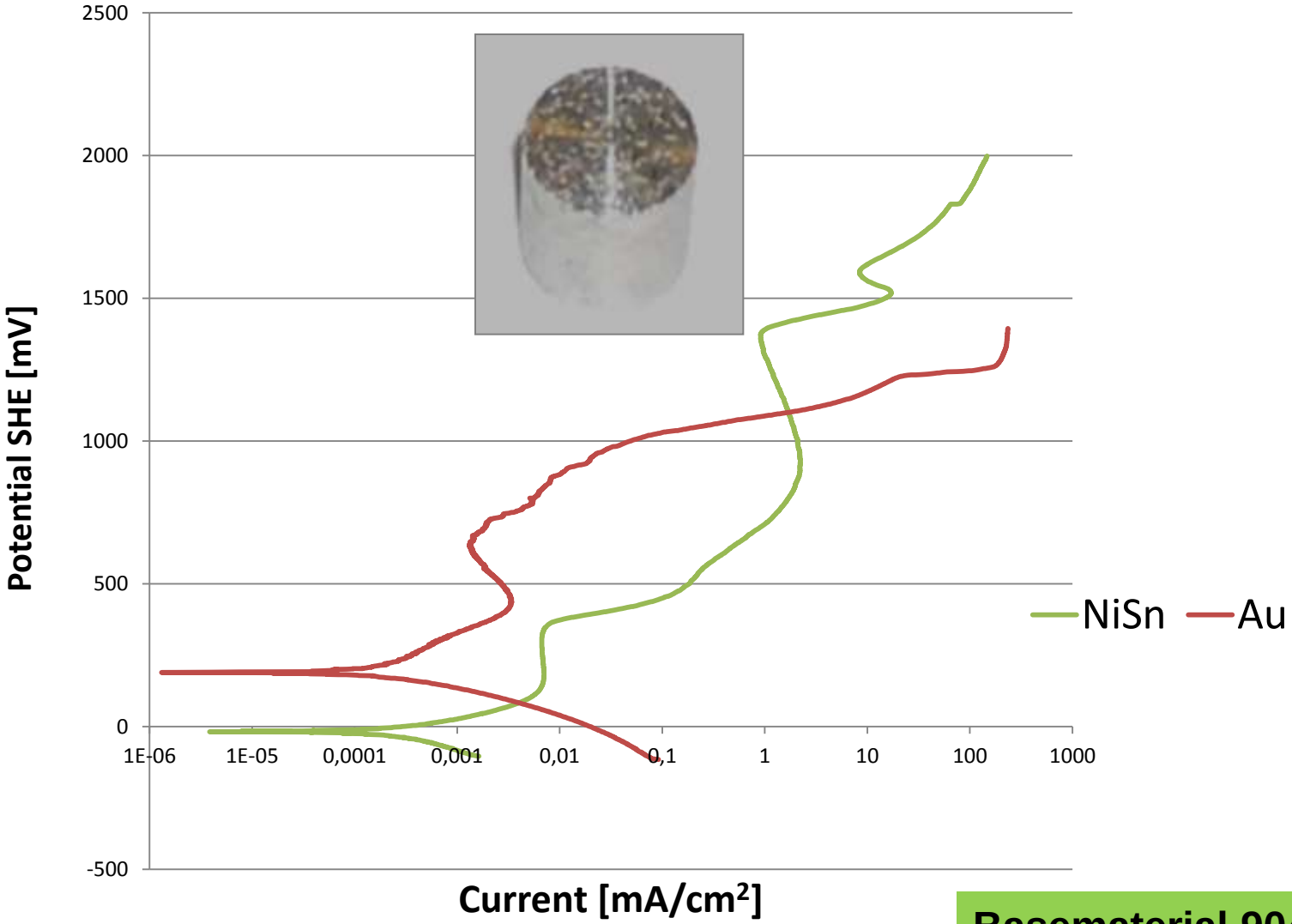
About 0.1 µA/cm^2

Polarization curves for tin/nickel

Test solution 3% NaCl in an acetate buffer pH = 6

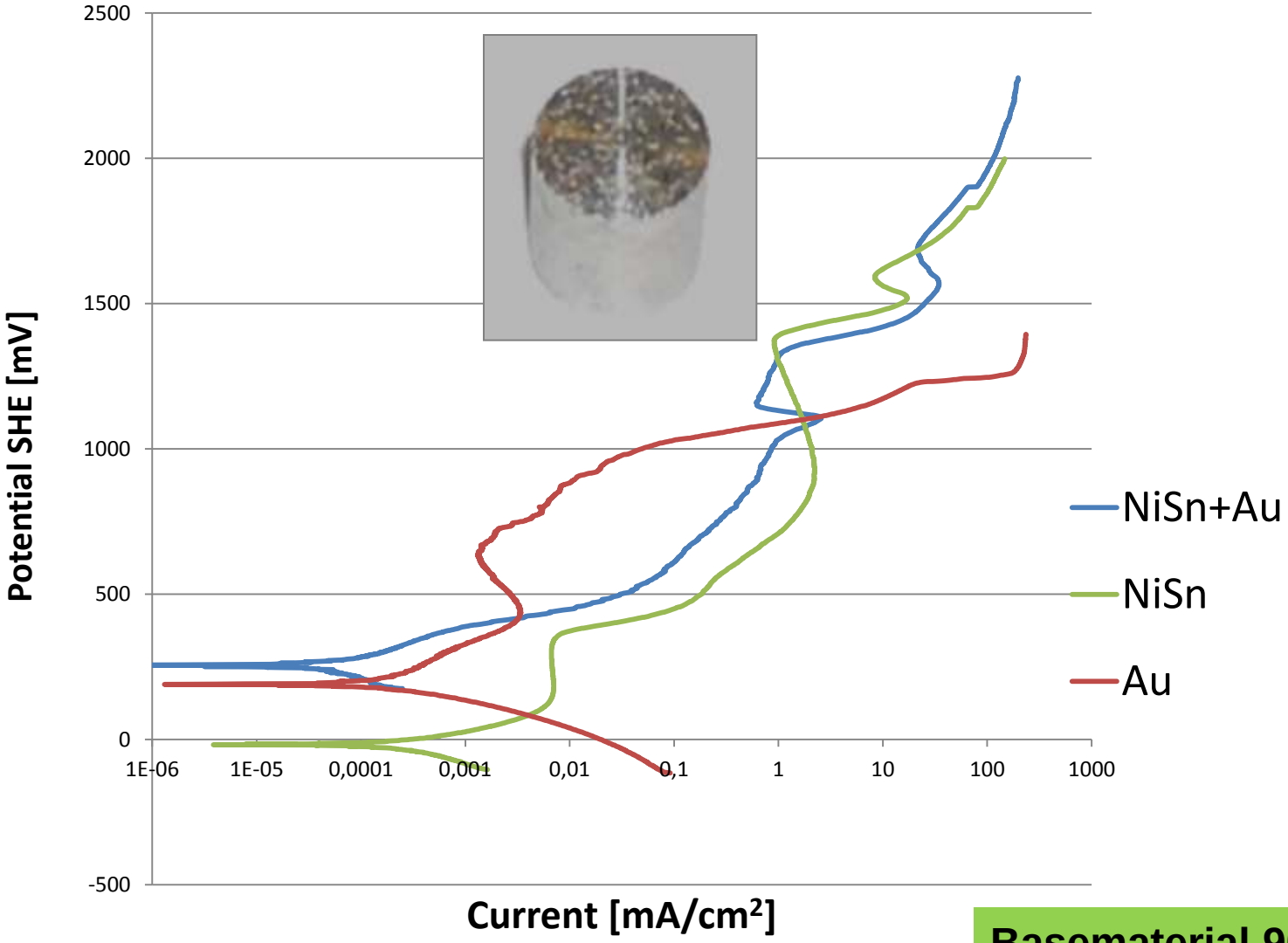


Polarization curves for tin/nickel & gold



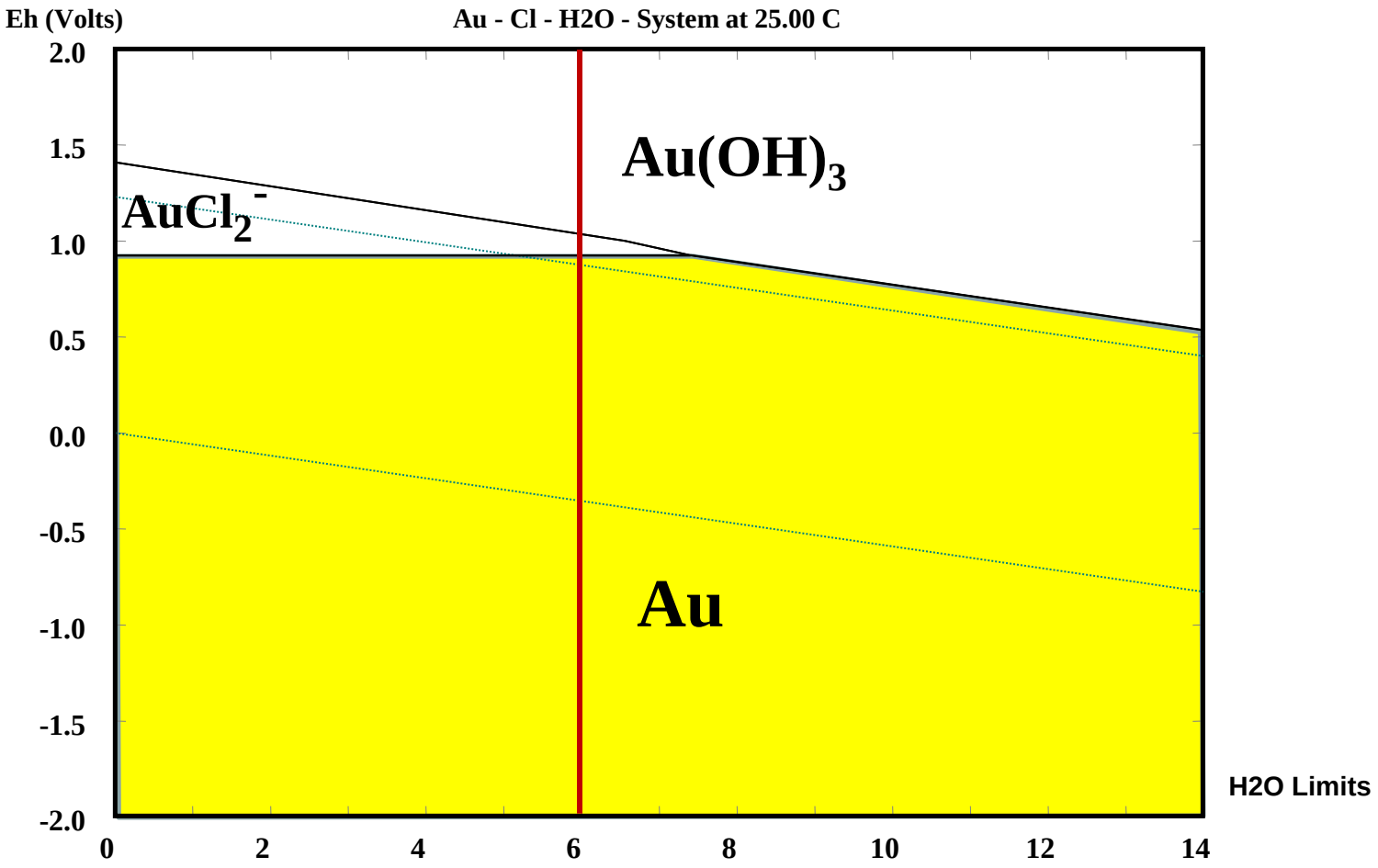
Basematerial 904

Polarization curves for tin/nickel & gold



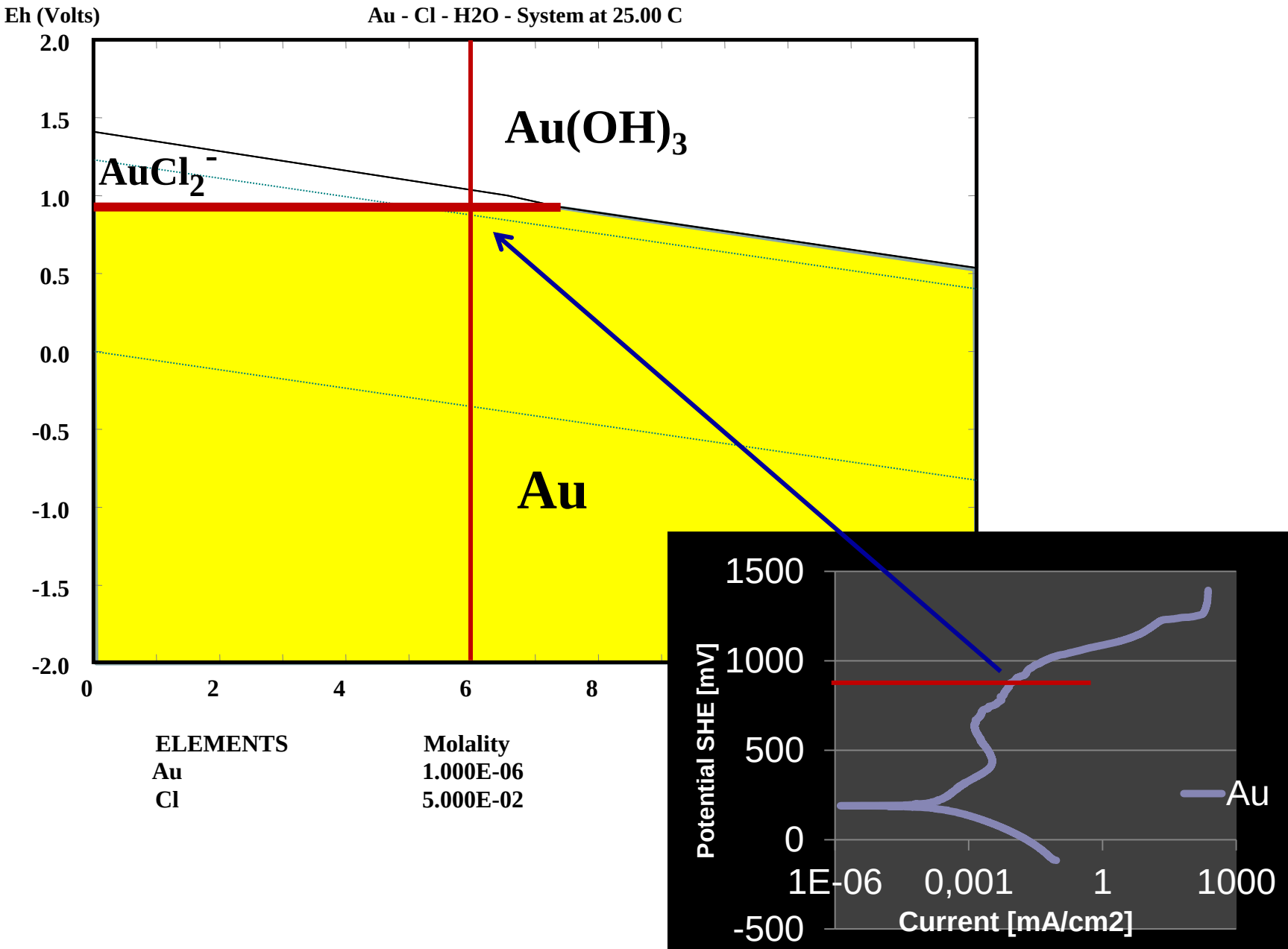
Basematerial 904

Multielement Pourbaix diagramme for gold and chloride



ELEMENTS	Molality	Pressure
Au	1.000E-06	1.000E+00
Cl	5.000E-02	1.000E+00

Multielement Pourbaix diagramme for gold and chloride



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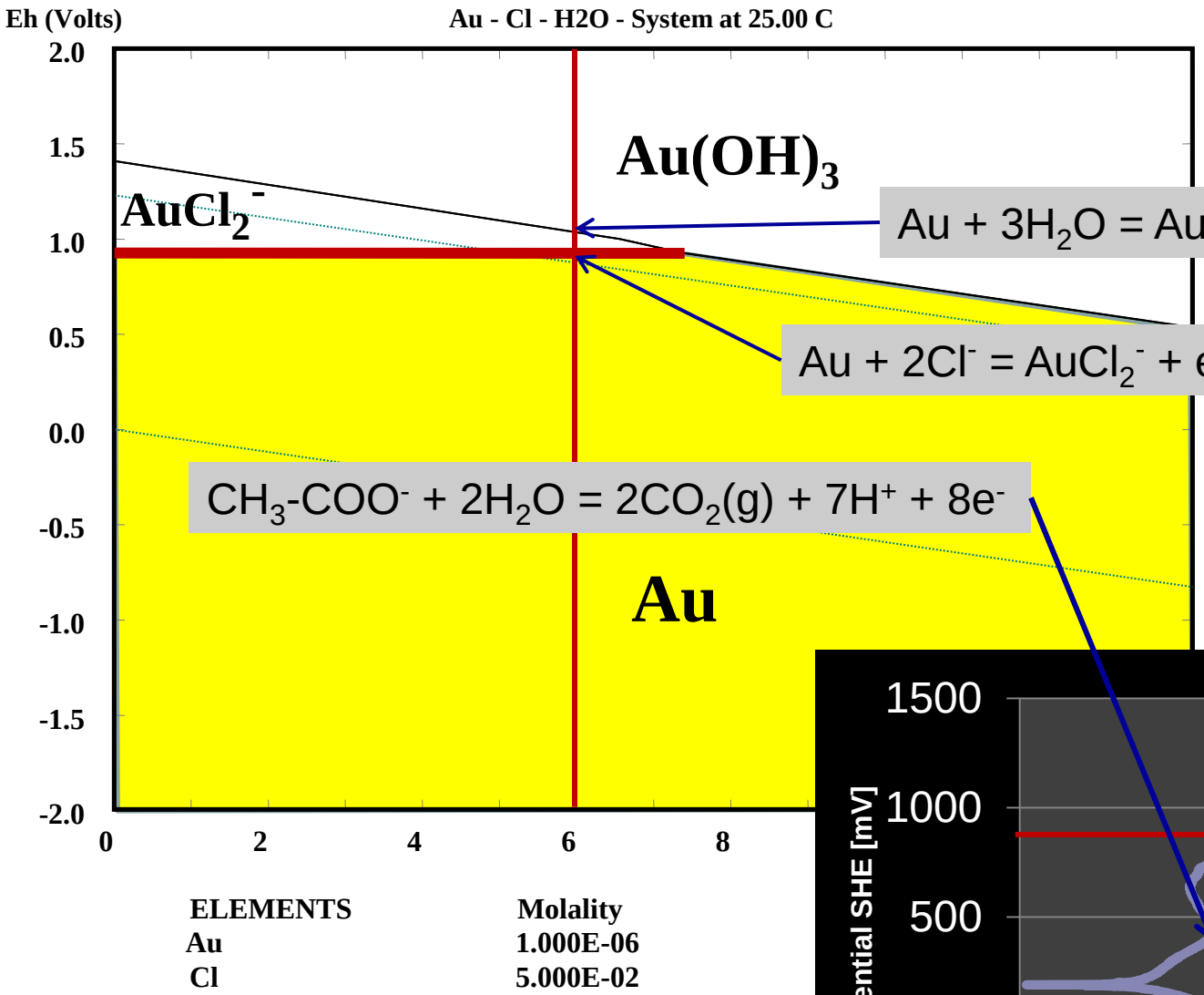
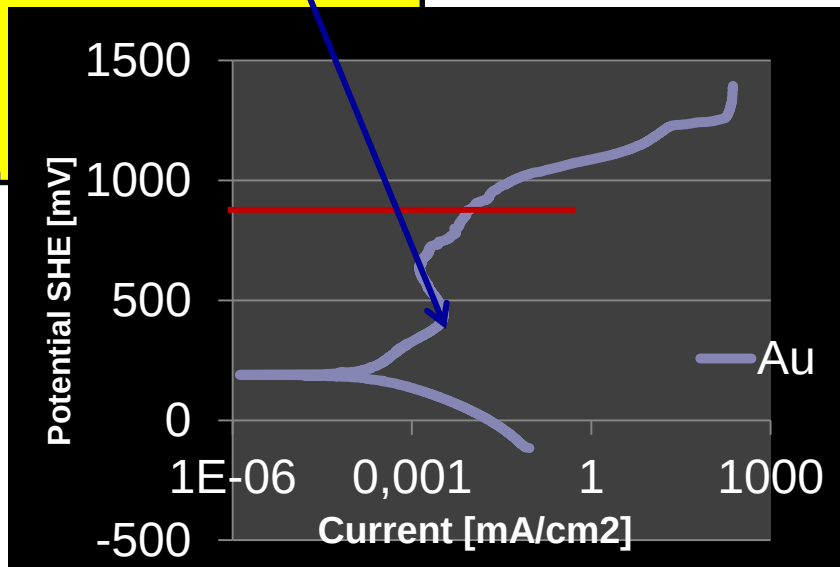


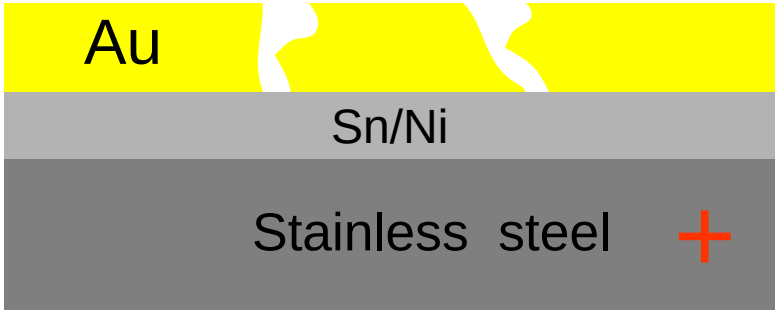
$Au + 3H_2O = Au(OH)_3 + 3H^+ + 3e^-$

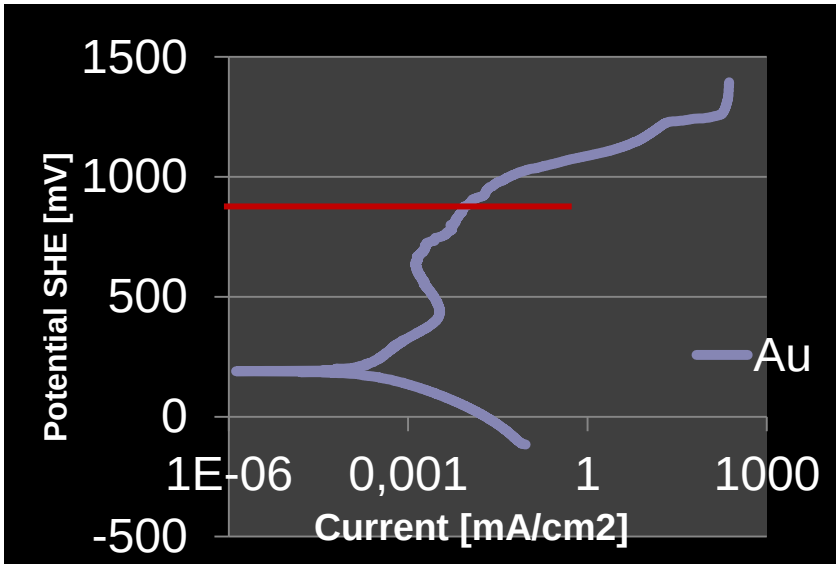
$Au + 2Cl^- = AuCl_2^- + e^-$

$CH_3\text{-}COO^- + 2H_2O = 2CO_2(g) + 7H^+ + 8e^-$

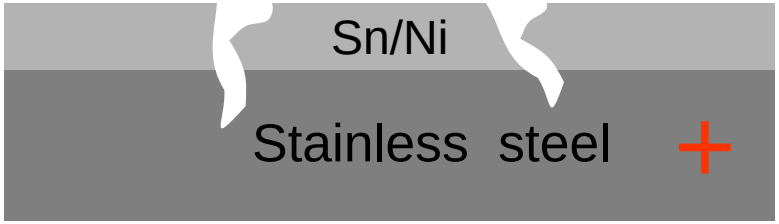


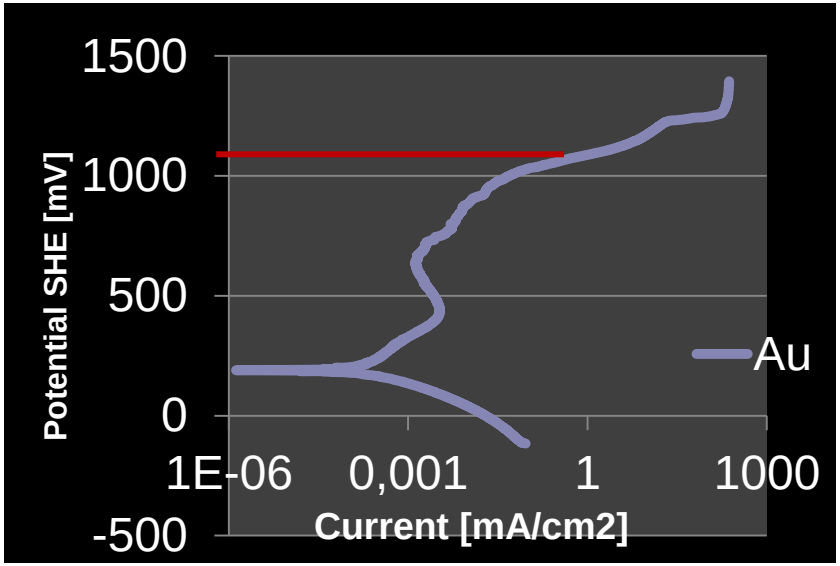
Polarization of the gold layer





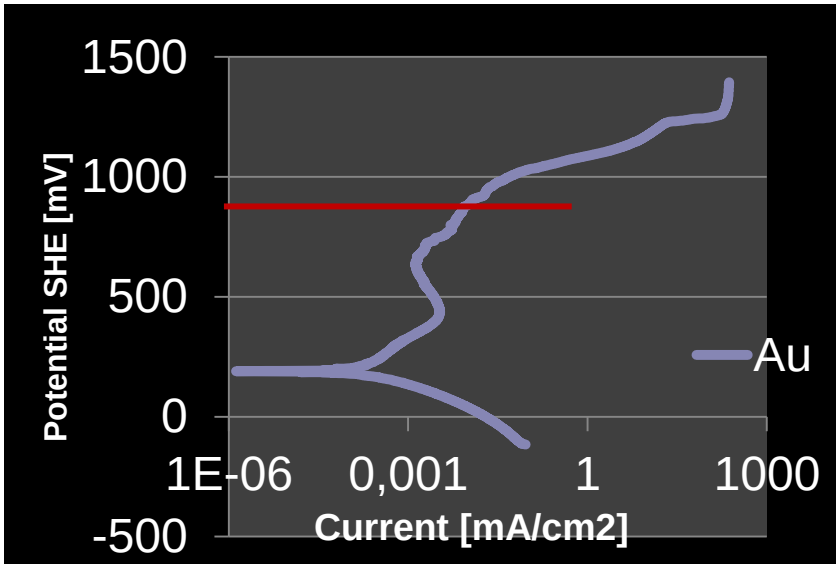
Polarization of the gold layer





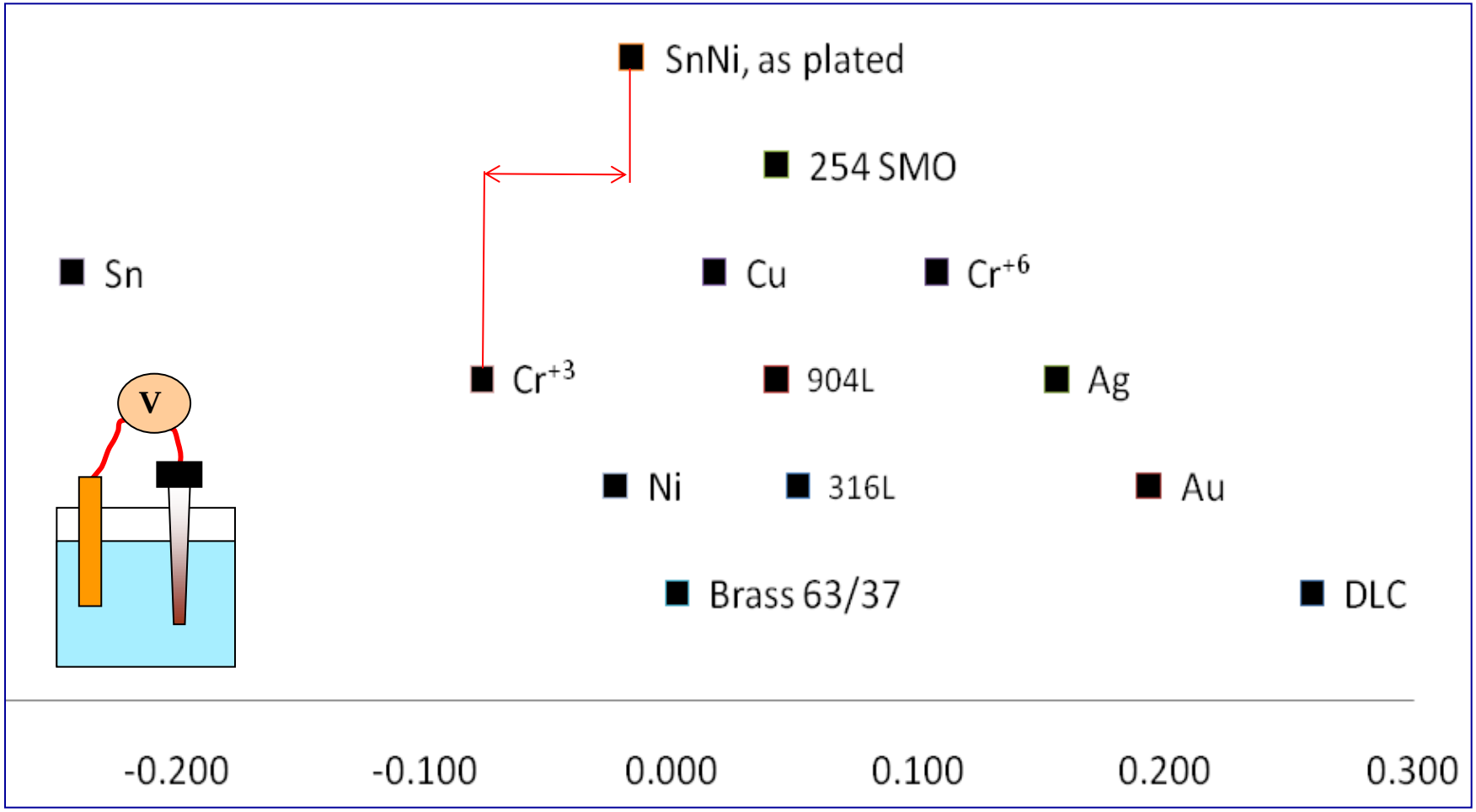
Polarization of the gold layer

The gold layer is stripped over time from the tin/nickel coating during the anodic polarization of the work electrode. In the third last pictures (to the right) the potential is close to +1000 mV (SHE) and the gold coating starts to corrode, forming colloidal $Au(OH)_3$ which start to discolor the work electrode.

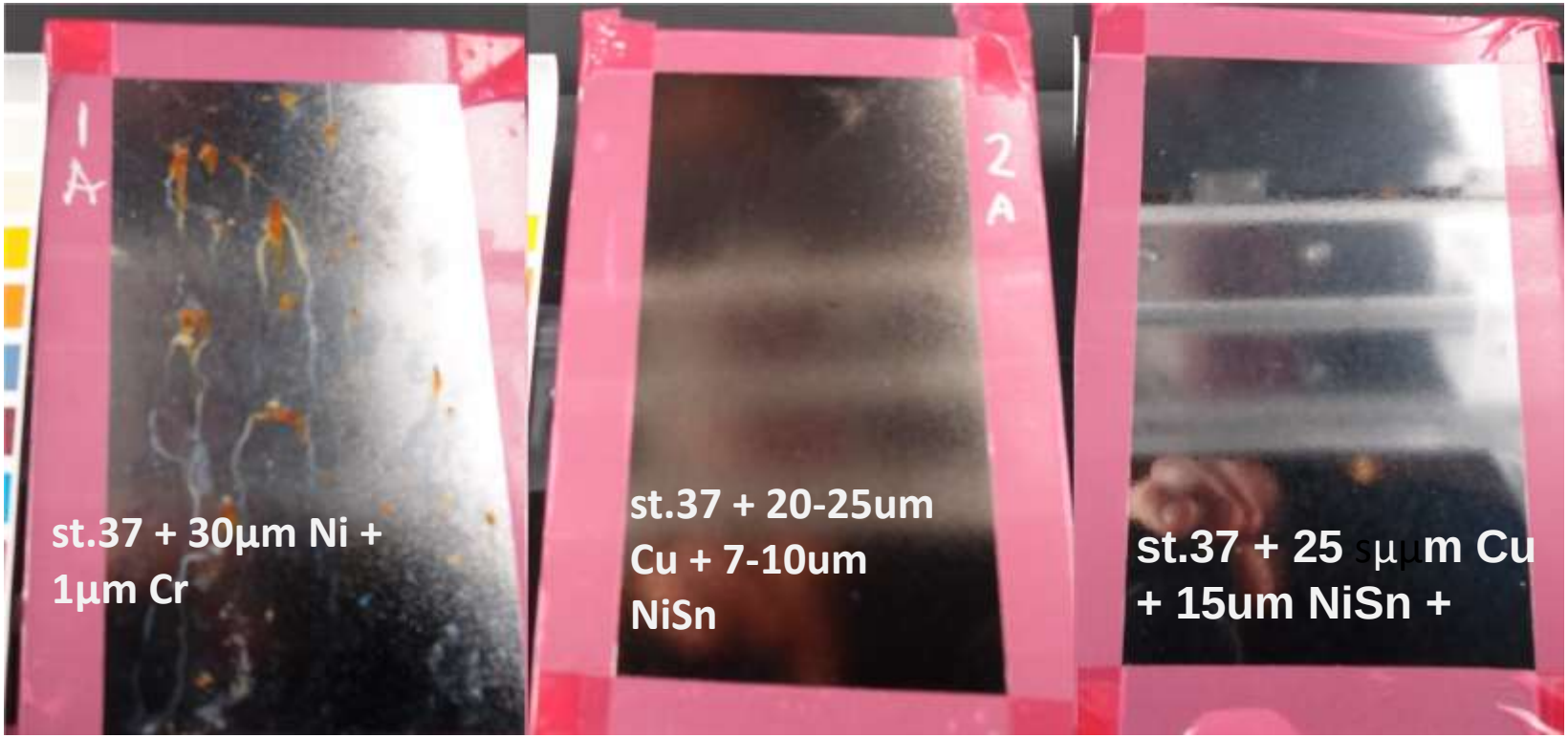


Saltspray tests

Corrosion potential of Tin/Nickel alloy compared with selected metals.



Salt spray, week 1

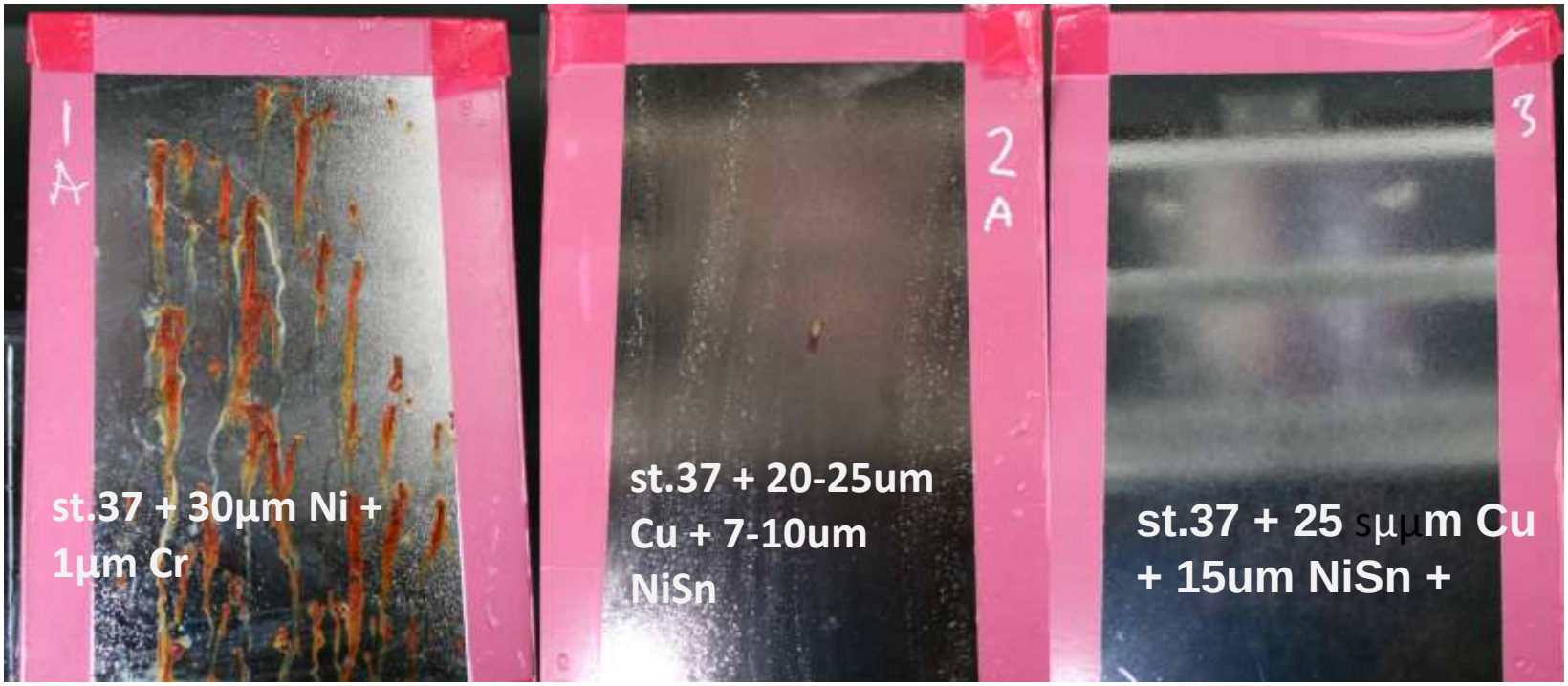


Cr on Ni

NiSn on Cu

Cr on NiSn

Salt spray, week 2



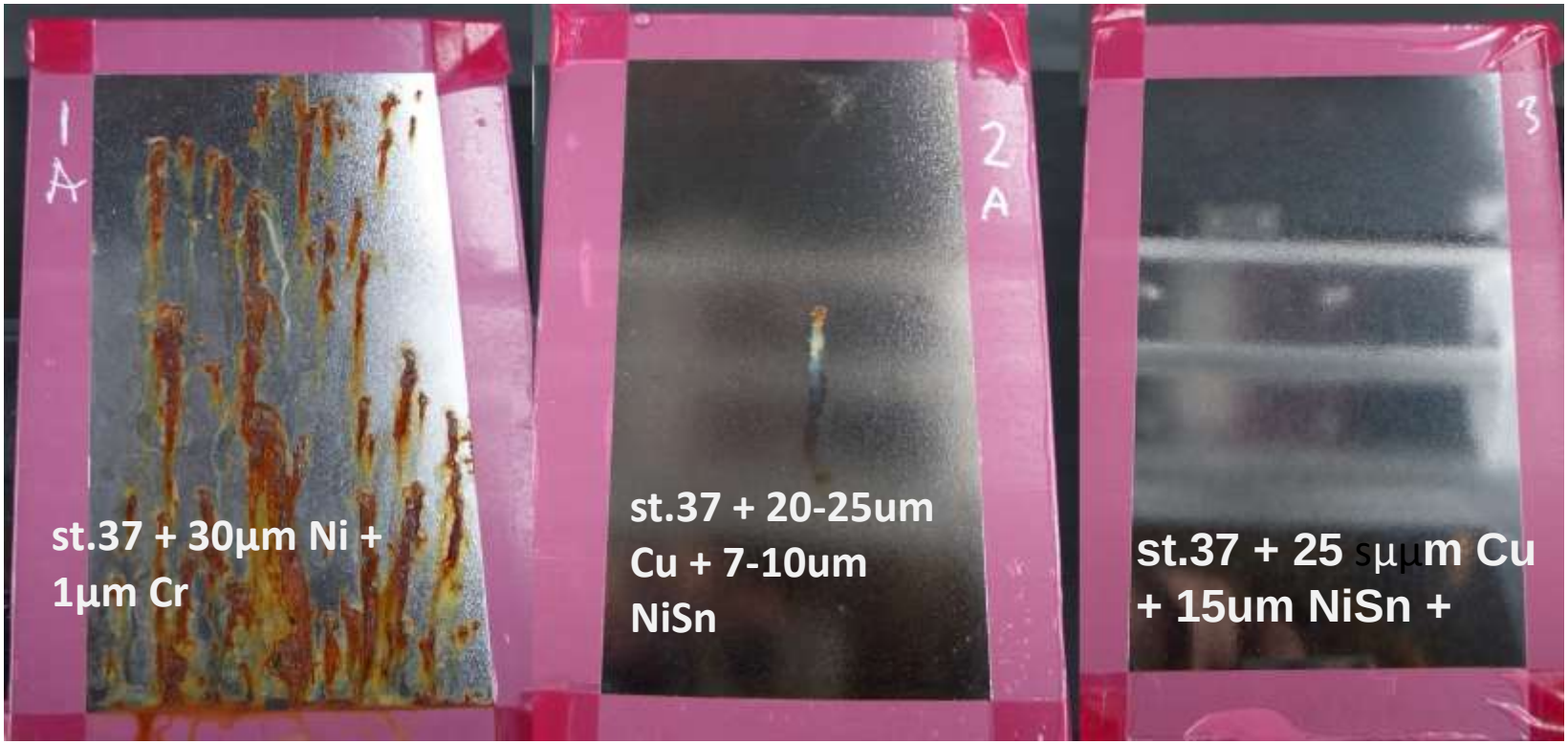
Cr on Ni

NiSn on Cu

Cr on NiSn

Salt spray, 19 days

After 4 months no corrosion



Cr on Ni

NiSn on Cu

Cr on NiSn

Conclusion

- Sn/Ni coatings cannot introduce nickel dermatitis
- The structure of electrodeposited equiatomic NiSn alloy was indicated in an X-ray diffraction pattern to mainly consist of a hexagonal structure of the NiAs type.
- Electrochemical results show that NiSn has a passive behaviour that exceeds that of stainless steel (904) in chloride electrolytes.
- Sn/Ni only give slow corrosion or none by galvanic coupling even with gold.
- Sn/Ni can be coated with Cr with good covering power using a new patented process and in this way replacing conventional bright chromium plating.

Questions