

Fundamentals of Electrochemistry:

The Electrolytic Polishing of metals. Application to Copper and Niobium

V. Palmieri

ISTITUTO NAZIONALE DI FISICA NUCLEARE

Laboratori Nazionali di Legnaro

and

UNIVERSITÀ DEGLI STUDI DI PADOVA

Science Faculty – Material Science Dept.

**A surface contaminant can be defined
as any material on a substrate**

- that interferes with any process involving the surface,*
- affects the surface properties in an undesirable way,*
- or influences the surface stability in an undesirable way*

Polishing is the reduction To an acceptable level

of Surface Contamination or of surface damaged layer

in order to have no significant amount

of undesirable material

A Major Concern In Processing:

**The Variability Of The Contamination Is
What Mainly Affects Cleaning
Reproducibility**

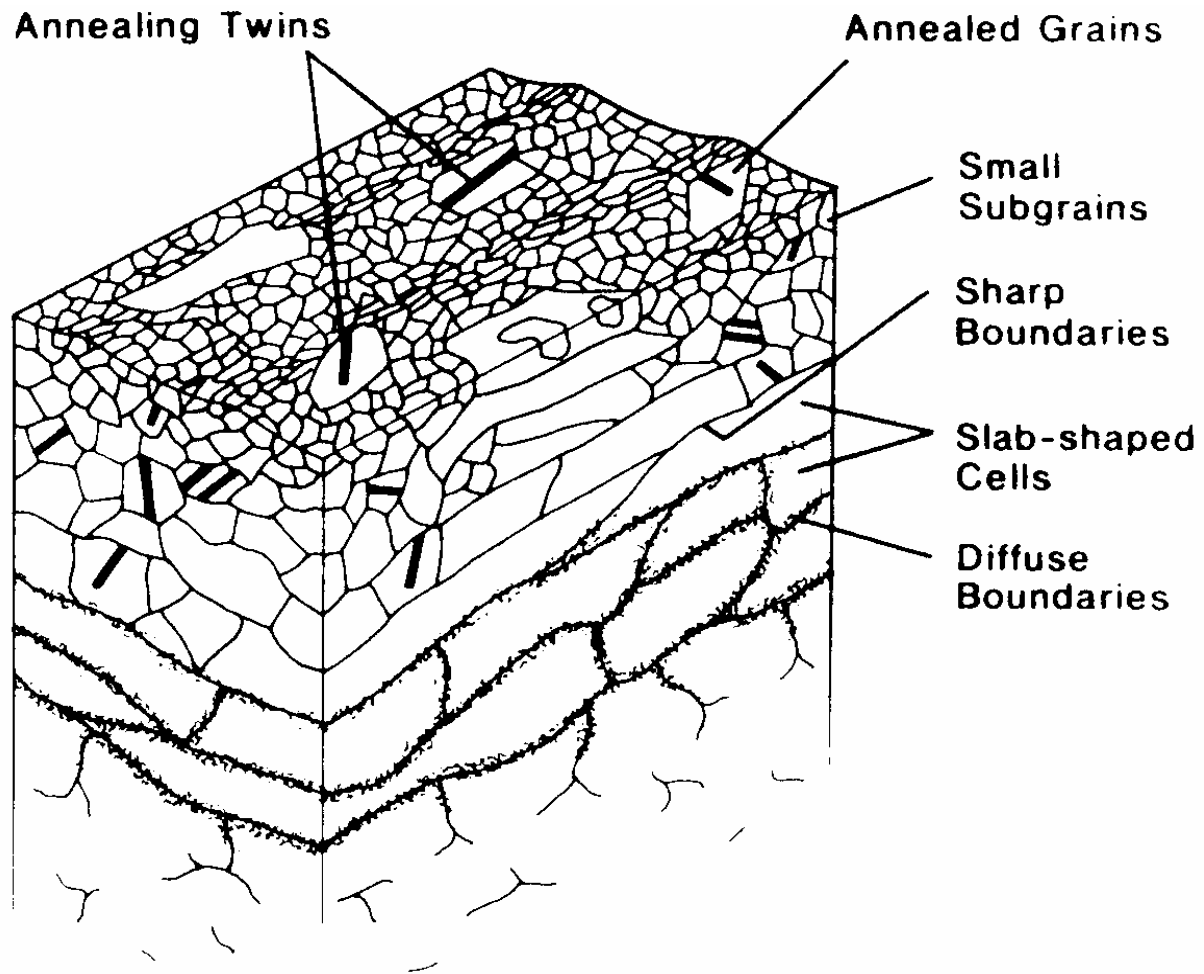
First Rule of Polishing techniques:

**NOT CONTROLLING
CONTAMINATION**

Means

***NOT CONTROLLING
CLEANING***

*Schematic sketch of the structure observed for an abraded OFHC Copper surface
(after Turley and Samuels; J Iron and Steel Inst, 186 (1957) 211)*



THE POLISHING SYSTEM

- 1. ABRASIVE CLEANING, GRINDING and MECHANICAL POLISHING**
- 2. SOLVENT CLEANING: Chlorofluorocarbons and Liquid CO₂**
- 3. SEMI-AQUEOUS CLEANERS: Terpenes; Alcohols; Ketones; Esters; Amines**
- 4. ULTRASONIC CLEANING**
- 5. MEGASONIC CLEANING**
- 6. SAPONIFIERS, SOAPS, AND DETERGENTS**
- 7. WIPE-CLEAN**
- 8. SUPERCRITICAL FLUIDS**
- 9. CHEMICAL ETCHING**
- 10. ELECTROCHEMICAL POLISHING**
- 11. ELECTROLESS ELECTROLYTIC CLEANING**
- 12. DEBURRING: laser vaporization, thermal pulse flash deburring**
- 13. STRIPPABLE COATINGS**
- 14. OUTGASSING**
- 15. REACTIVE CLEANING: Anodic Oxidation and subsequent removal of the oxide**
- 16. OZONE CLEANING**
- 17. HYDROGEN CLEANING**
- 18. REACTIVE PLASMA CLEANING AND ETCHING**
- 19. PLASMA CLEANING**
- 20. SPUTTER CLEANING**
- 21. ION BEAM CLEANING**

Suggested readings on Electropolishing:

IMPROVED SURFACE TREATMENT OF THE SUPERCONDUCTING TESLA CAVITIES

**L. Lilje, C. Antoine, C. Benvenuti, D. Bloess,
J.-P. Charrier, E. Chiaveri, L. Ferreira, R. Losito,
A. Matheisen, H. Preis, D. Proch, D. Reschke, H. Safa,
P. Schmueser, D. Trines, H. Wenninger**

DESY, Notkestrasse 85, D-22607 Hamburg, Germany

CEA Saclay, DAPHNIA, 91191 Gif-sur-Yvette, France

CERN, CH-1211 Geneva 23, Switzerland

Universitaet Hamburg, Notkestr. 85, D-22607 Hamburg, Germany

This Workshop:

PROGRESS OF Nb/Cu TECHNOLOGY WITH 1.5 GHZ CAVITIES

S. Calatroni, E. Barbero-Soto, C. Benvenuti, L. Ferreira, H. Neupert,
CERN, Geneva, Switzerland

Abstract

The residual resistance of Nb/Cu cavities exponentially at high RF field. Two main possible causes have been investigated in detail: the hydrogen incorporated in the film during the sputtering process and the roughness induced by the substrate. The latter has been reduced with **an optimised electropolishing technique**, which couples laboratory analyses of the electrical characteristics of the bath with numerical simulations of the actual process. The hydrogen content of the film can be reduced by increasing the pumping speed during deposition, either in the form of a suitable getter underlayer or of an appendage getter pump. The main results from these studies will be presented, together with other minor developments.

ALTERNATIVE APPROACHES FOR SURFACE TREATMENT OF Nb SUPERCONDUCTING CAVITIES

C. Z. Antoine, A. Aspart, J.P. Charrier, H. Safa, B. Visentin,
CEA, DSM/DAPNIA/Service d'Etude des Accélérateurs,
CE-SACLAY, F-91 191 Gif-sur-Yvette Cedex

Abstract

With improvements in fabrication and ultra cleanliness techniques, the limitation on SC cavity performance now seems to be the surface state generated by the etching process. The influences of various surface treatments are now being studied at several laboratories (KEK, DESY, CERN...). This paper presents the results obtained at Saclay, mainly on cavities, along with surface studies conducted on Niobium samples (morphology, surface composition).

ENGINEERING SOLUTIONS FOR THE ELECTRO-POLISHING OF MULTI-CELL SUPERCONDUCTING ACCELERATOR STRUCTURES

E.Schulz; R.Bandelmann, K.Escherich, D.Keese, M.Leenen, L.Lilje, A.Matheisen, H.Morales, P.Schmüser, M.Seidel, N,Steinhau-Kühl, J.Tiessen

Deutsches Elektronen Synchrotron DESY, Notkestraße 85, 22607 Hamburg

Abstract

Due to surface treatment with electro-polishing superconducting niobium resonators can potentially reach accelerating gradients well beyond 35 MV/m at a frequency of 1.3 GHz. The anticipated gradient for the 500GeV version of the TESLA collider is 23.4 MV/m. In view of the extendibility of the collider towards higher energies this technology is therefore of great importance for the TESLA project.

This Workshop:

Development of Hydrogen-free EP and Hydrogen Absorption Phenomena

T. Higuchi, K. Saito

Grad . Univ. Advanced Studies; KEK Accelerator Laboratory

Abstract

We developed a hydrogen-free electropolishing method for superconducting Nb cavities.....

....We prevent hydrogen absorption in barrel polishing **replacing the water from a liquid without hydrogen component.....**

.....Thus we finally invented the hydrogen-free electropolishing **by putting one drop of Nitric acid into the EP acid**

THE ELECTROLYTICAL POLISHING

History's first reference to electropolishing: 1912

The Imperial German Government issued a patent for the finishing of Silver in a cyanide solution.

No advancement was made until 1935, when Copper was successfully electropolished.

1936 and 1937 Charles Faust electropolishes Stainless Steel.

During World War II, both Allied and Axis scientists yielded a substantial number of new EP formulas. Data produced in this period were published in hundreds of papers during the immediate post-war.

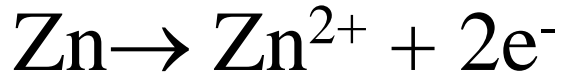
Dozens of paper were registered in that same period

An **anode** is an electrode on which an oxidation reaction is occurring

A **cathode** is an electrode on which a reduction reaction is occurring

Anodic Reactions

- Examples



zinc corrosion



iron corrosion



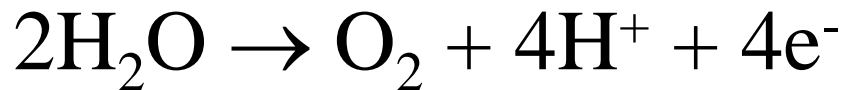
aluminium corrosion



ferrous ion oxidation



hydrogen oxidation



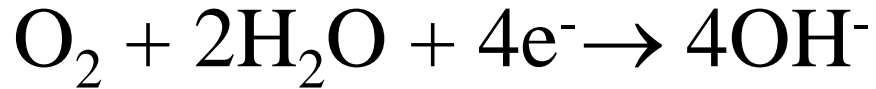
oxygen evolution

- Oxidation reactions

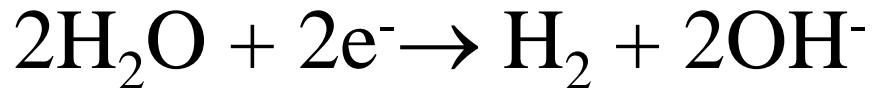
- Produce electrons

Cathodic Reactions

- Examples



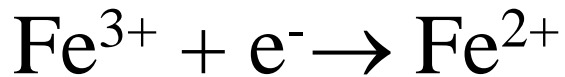
oxygen reduction



hydrogen evolution



copper plating



ferric ion reduction

- Reduction reactions

- Consume electrons

ANODIC REACTIONS IN ELECTROLYTIC POLISHING

depending mainly on the nature of:

- The dissolving metal,
- The electrolyte composition,
- The temperature,
- The current density,
- The degree of agitation

The following reactions may take place:

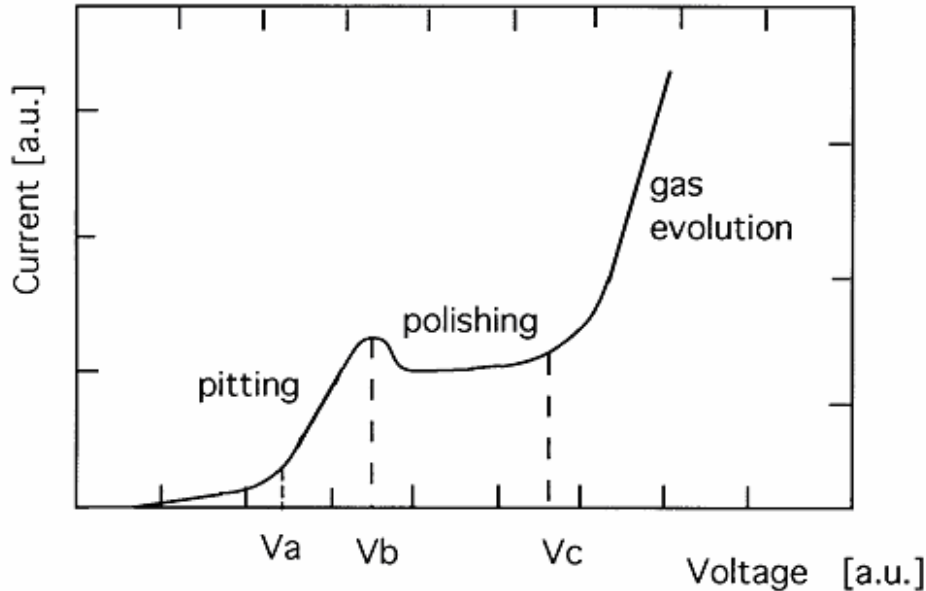
- 1) Transfer of metal ions into the solution $\text{Me} = \text{Me}^{2+} + 2\text{e}^-$
- 2) Formation of oxide layers: $\text{Me} + 2\text{OH}^- = \text{MeO} + \text{H}_2\text{O} + 2\text{e}^-$
- 3) Evolution of oxygen: $4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$.
- 4) Oxidation of various components of the solution. $\dots = \dots$

The electrolytes used in electropolishing should satisfy a number of requirements:

For instance:

- 1) the electrolyte should contain complex ions;
- 2) the electrolyte should contain anions with large radii and a small charge, e.g., ClO_4^- , H_2PO_4^- , $\text{H}_3\text{P}_2\text{O}_7^-$, etc.
- 3) a viscous liquid layer should be formed on the anode during the process.

Current density vs. voltage for Copper electropolishing in phosphoric acid



Up to the point V_B the surface conserves its mechanically worked appearance and shows some signs of pitting.

Fluctuations in both voltage and current and a simultaneous drop in current density are found just after V_B .

Over the horizontal range ($V_B - V_C$), the current density remains constant although the voltage increases; A polishing effect is observed between V_B and V_C , **but the best results are obtained near point V_C .**

P.A. Jacquet; Metal Finishing 47 (5) (1949) 48

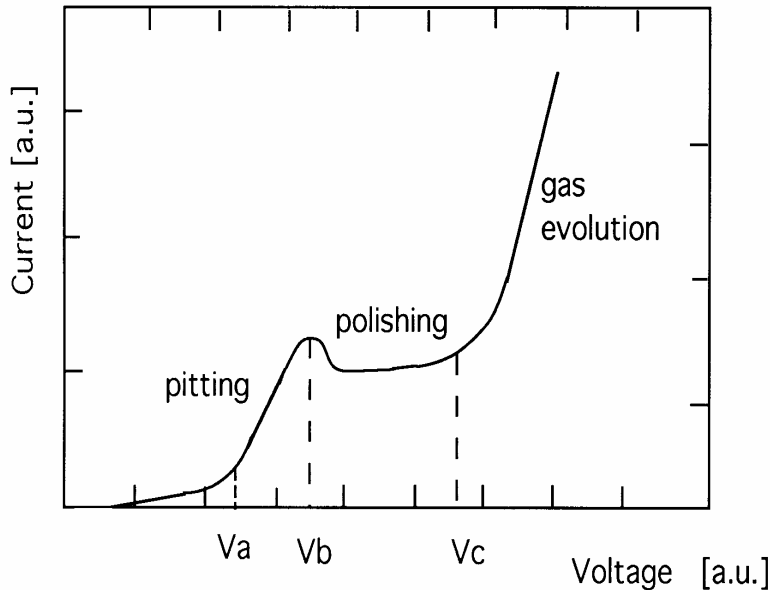
The first bubbles of gaseous oxygen appear on the anode at a voltage corresponding to point V_C .

A well polished surface is obtained over section V_C , at higher voltages, the dissolution of metal is accompanied by evolution of oxygen, but there is some pitting as a result of contact with oxygen bubbles trapped on the surface

At potentials much higher than V_C the quality of polishing improves, **since the oxygen bubbles cannot be trapped on the surface and there is no pitting**

A solid, brown film is formed on the anode surface for voltages between V_A and V_B , the film adheres to the metal but is destroyed at higher current densities.

The thin layer of electrolyte in the vicinity of the anode assumes a bluish color



*Moderate agitation of the solution reduces the thickness of the bluish layer **while voltage drops.***

*Vigorous agitation reduces the thickness to a few tenths of a μm . **Voltage drops even more.***

Jacquet assumed that a relationship exists between the formation of the viscous layer in the electrolyte and the polishing effect.

According to Jacquet, the process should be controlled by maintaining a constant voltage rather than a constant current density; in this case it is not necessary to calculate the total surface area of the sample to be polished.

Rigorously speaking, it would be not possible to control the electropolishing process solely on the basis of voltage or current density measurements,

*The **Applied Voltage V** is a function of the **anode** and **cathode potentials**, the **Voltage Drop in the electrolyte ($I R_{electr}$)** and the **voltage drops in the conductors and contacts ($I R_{Conduct}$)**, i.e.*

$$V = (V_{anode} - V_{cathode}) + I R_{electrol} + I R_{Conduct}$$

Thus V depends on:

- the electrode potentials,*
- the electrolyte concentration,*
- the anode and cathode surfaces,*
- the arrangement of electrodes in the bath*
- and the shape and size of the bath.*

Hence, the "applied voltage" used by Jacquet as a control parameter would not always correspond to the optimum polishing conditions

The electropolishing process could be controlled on the basis of the anode potential through the use of a special non-polarizing auxiliary reference probe (for ex. a saturated calomel third electrode)

On the other hand. the potentials of the anode and of the auxiliary electrode do not remain constant - they change as a function of the time of electrolysis and the composition of the electrolyte.

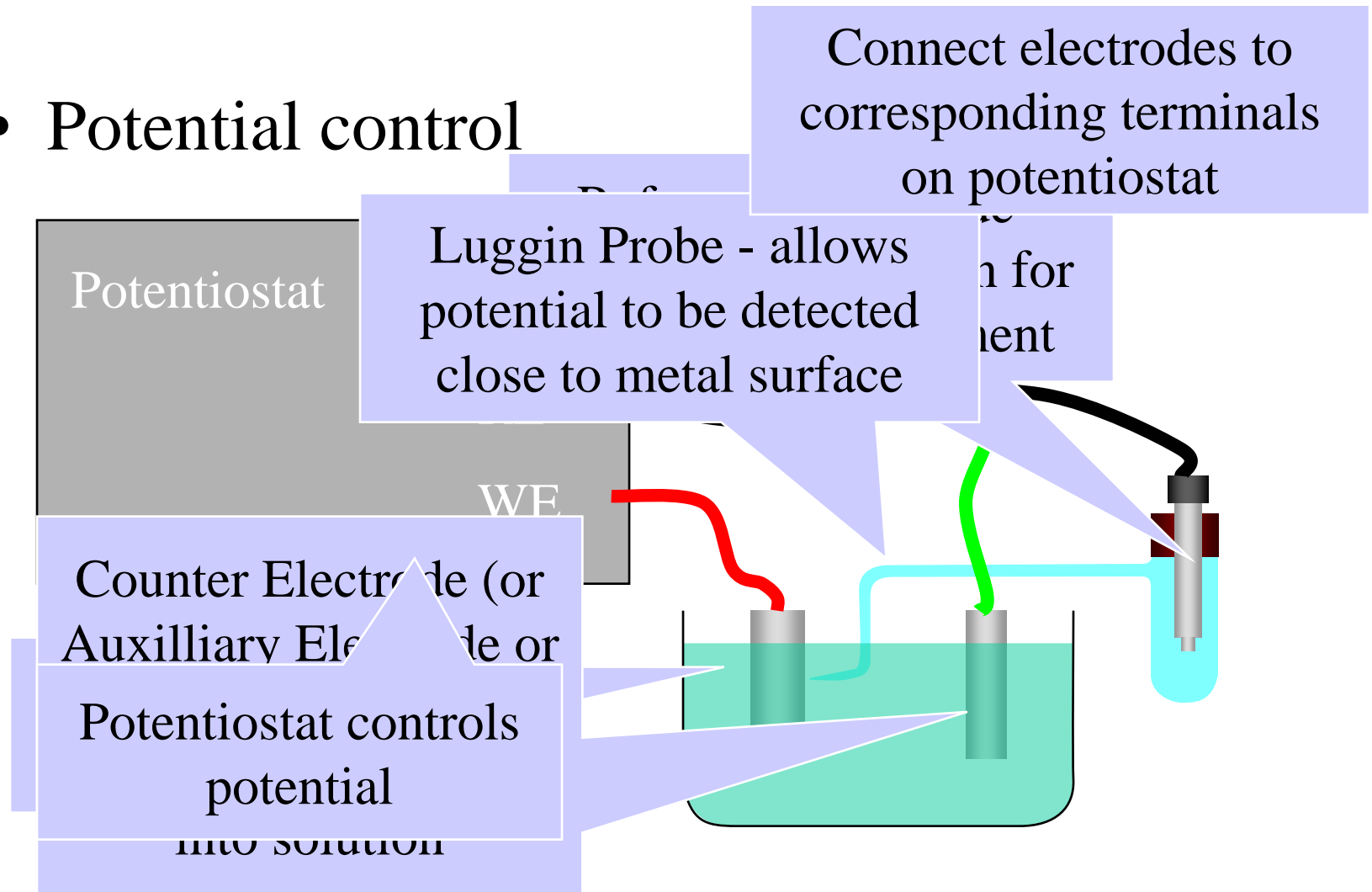
For this reason, the reading of the auxiliary electrode should be corrected from time to time.

Reference Electrode

- Commonly use Saturated Calomel Electrode (SCE)
- Properties may degrade with time (and misuse)
 - check one against another (should not be more than 1 to 2 mV difference)
 - do **not** pass current through the reference electrode (e.g. do not connect to working or counter electrode)
 - do not allow to dry out

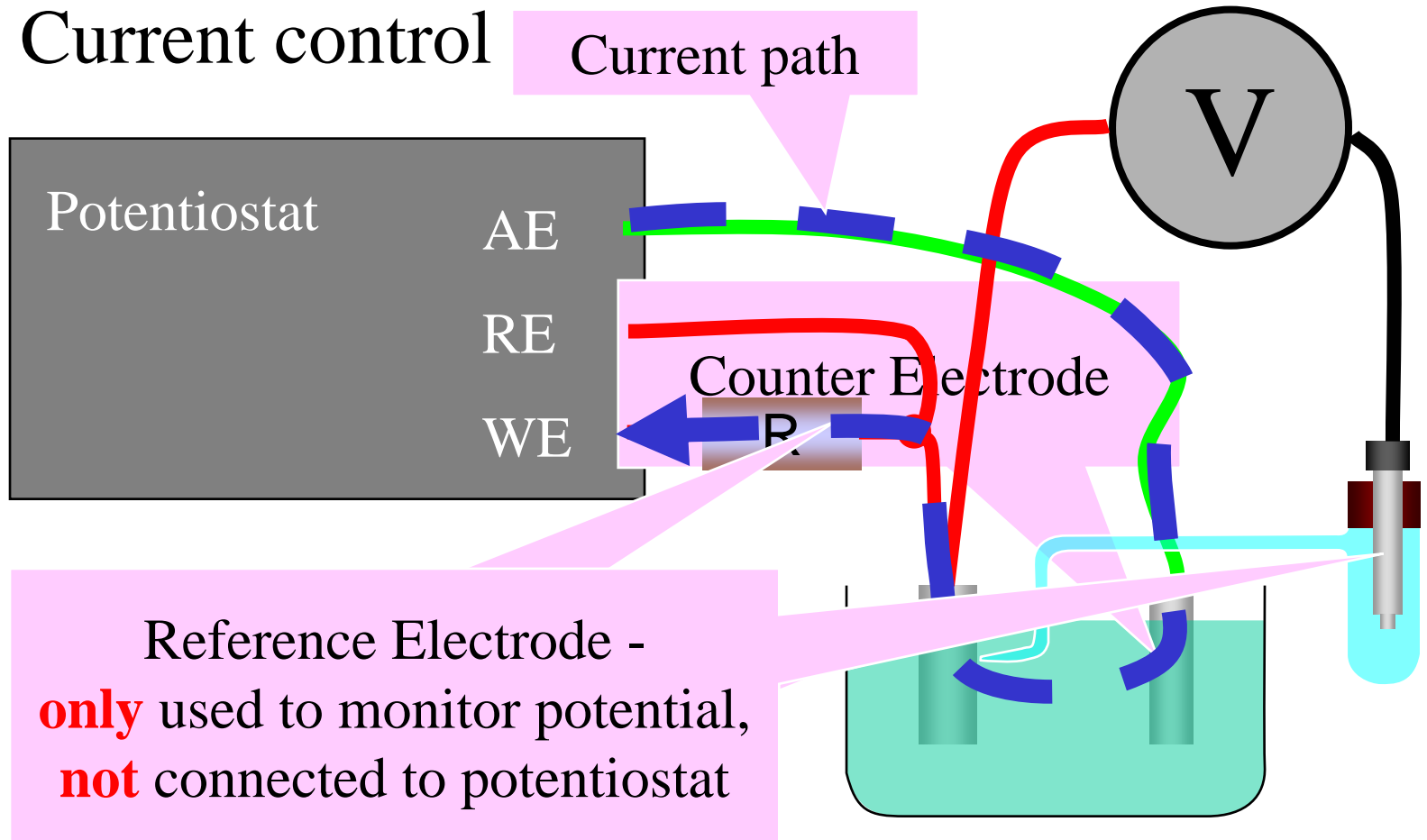
Measurement Methods

- Potential control



Measurement Methods

- Current control



Reference Electrode

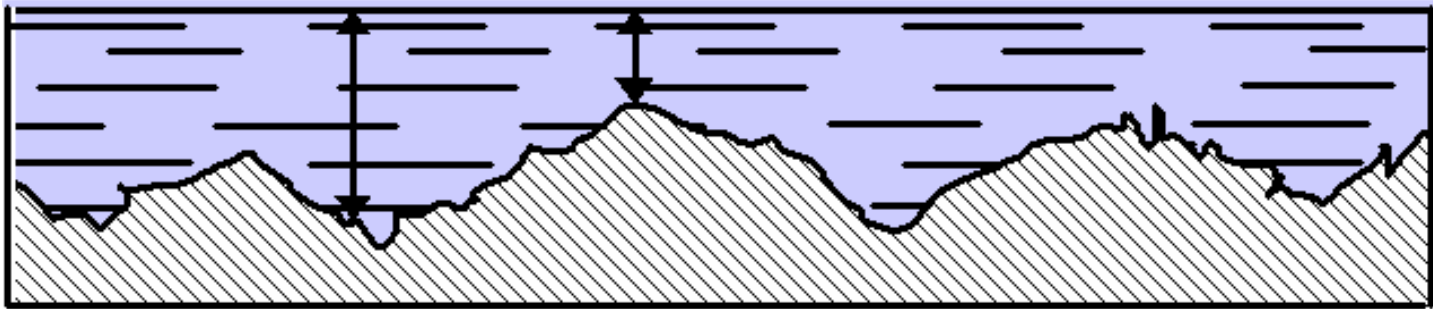
- Solution in SCE (or Ag/AgCl electrode) is saturated KCl
 - beware of chloride contamination of test solution by Cl^- leaking from reference electrode
 - make sure solution remains saturated

Jacquet proposed a simple mechanism for EP:

Jacquet, P.A., Trans. Electrochem Soc, 69, 629, (1936)

A **viscous layer** of anodic dissolution products is formed:

Respect to the bulk of the electrolyte, this layer has **higher viscosity** and **greater electrical resistivity**



- The thickness of the liquid **insulating** layer is greater in crevices than on projections.
- **The current density on projections it is higher than in crevices.**
- For this reason, projections dissolve more rapidly than crevices, and this produces a surface-leveling effect.

Search for the best polishing conditions:

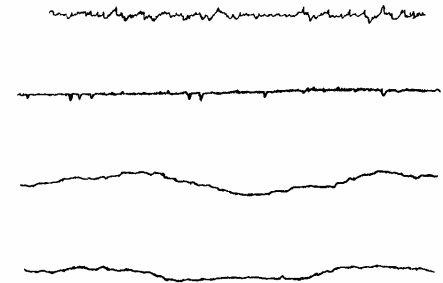
Manipulation of film build-up conditions in micro-EP

P. J. Lee

Applied Superconducting Center, University of Wisconsin-Madison

EP can be broken down in 2 different processes:

Macro-EP and **Micro-EP**



Great care must be paid for stable and controlled EP conditions. This is sometime impossible for multi-phase/elements materials.

A new method: **periodic cycles of macro-EP and micro-EP** by a right balancement of film dissolution and film creation.

Automatic control of plateau by locking on the minimum of differential conductivity

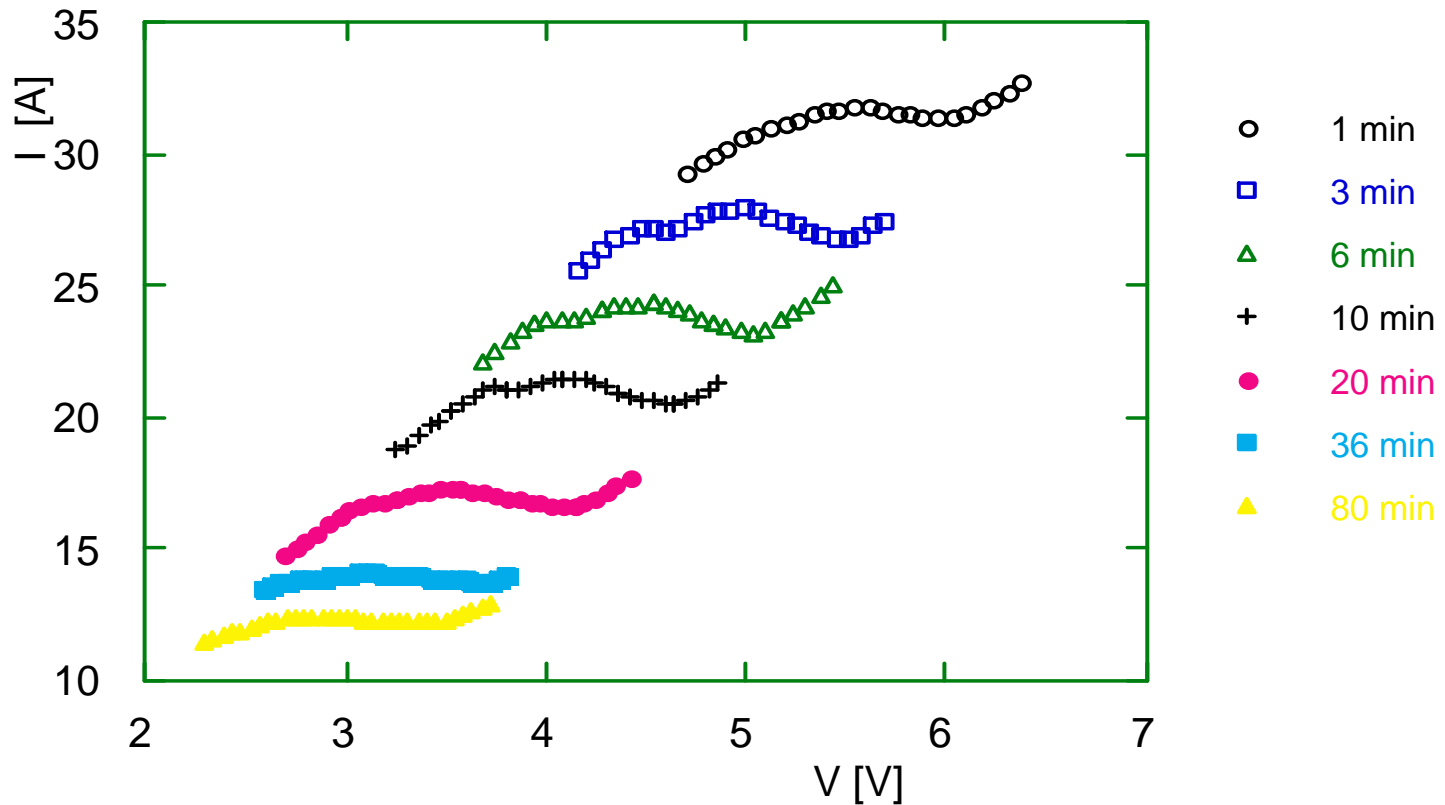
V. Palmieri, S. Stark, F. Stivanello, INFN-LNL

The I-V Polarization curve and its derivative are computer monitored

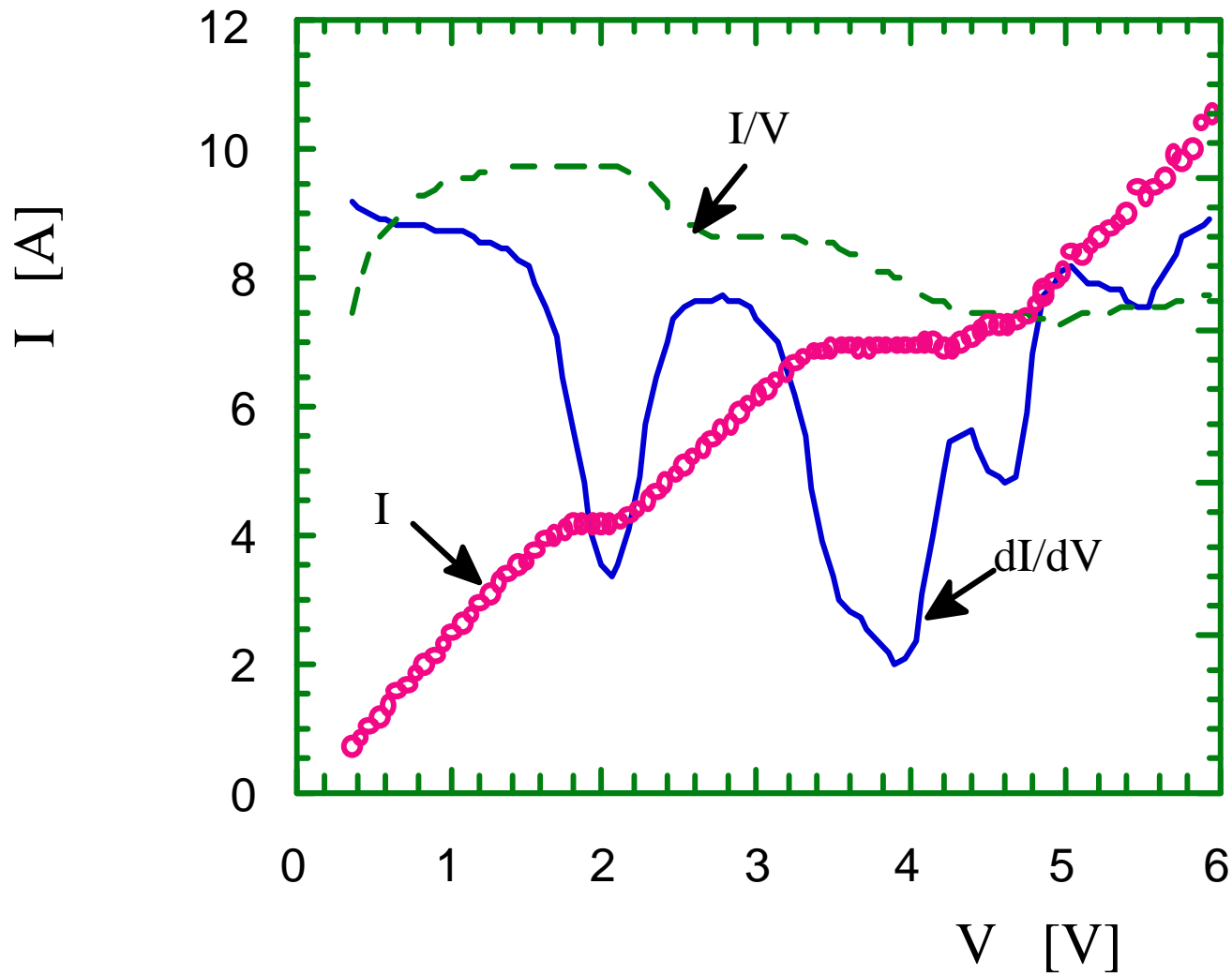
The working point is chosen as the minimum of the differential conductance of the bath, that corresponds to the point of maximum resistance of the viscous layer

(proceedings of Tsukuba SRF 2001)

The I-V characteristic evolves with time

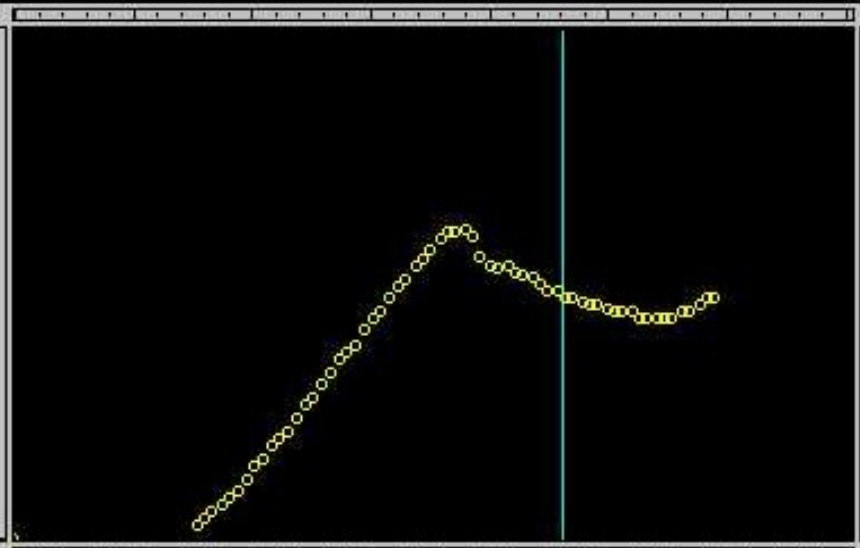


The voltage value corresponding to the minimum of differential conductance and the relative current value

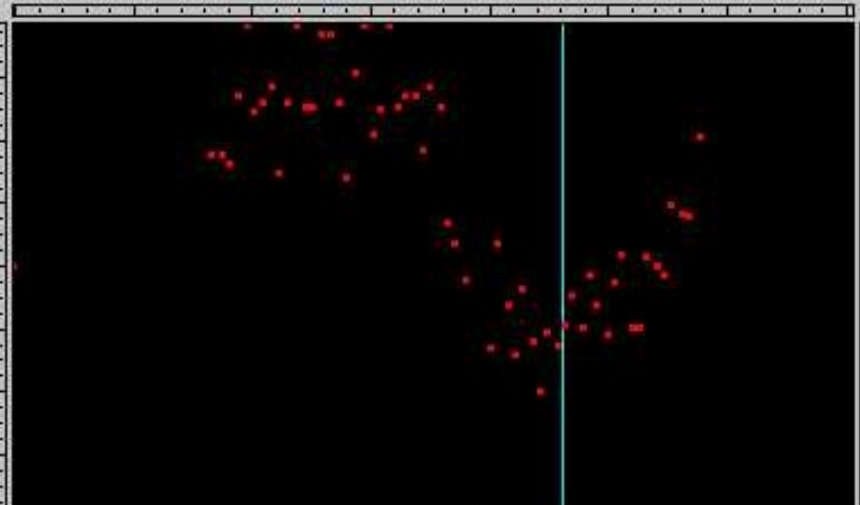


I-V characteristic for a Copper cavity (circles); Plot of the dI/dV (continuous line) and of I/V (shaded line) versus voltage

Current vs Voltage



Conductivity vs Voltage



00:20:54

2.31

V

New curve

.404

A

Auto

826.2

C

4.90E-1

um

The 5.93E-4 Plate QWR Cu has been chosen.

Umax

Imax

U

60.0

50.0

3.5



3.5

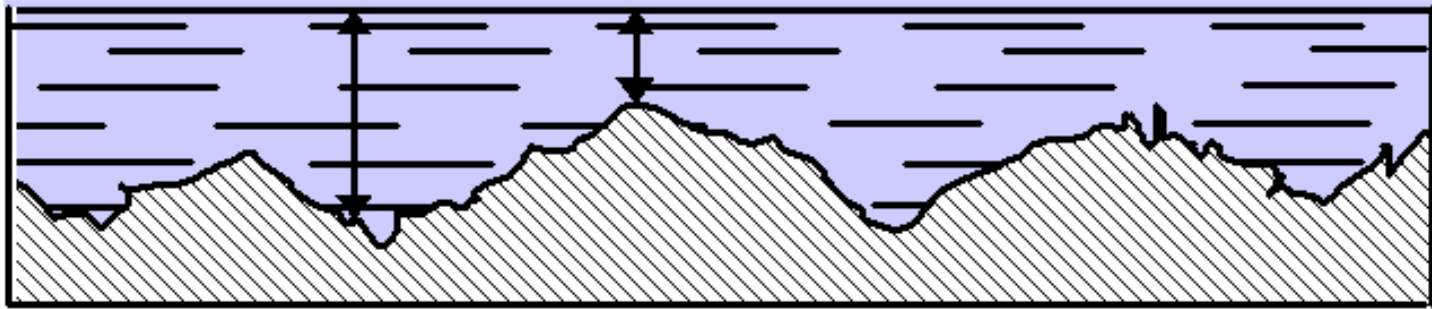
1.0

2.3



Typical table displayed on the computer screen controlling the electropolishing processes. The curve on the top left is the I-V characteristics; the curve on the bottom left is the derivative of current versus voltage. The numbers on the top-right are the process parameters; the knobs at the bottom-right are needed for settling the starting point

According to Elmore:



Surface leveling is due to the diffusion of anodic dissolution products from the anode through the film.

The dissolution rate is again higher from protrusions than from wells.

Elmore, W.C., J. Appl. Phys., 10, 724, (1939); 11, 797, (1940)

The "viscous film" theory of Jacquet and the diffusion theory of Elmore have much in common.

In fact, a viscous film really forms on the anode surface and diffusion and convection processes really occur at different rates on projections and crevices.

Jacquet attributes the leveling of rough surfaces to differences in the degree of "insulation" of peaks and crevices,

Elmore believes that the effect is associated with differences in the concentration gradients of metal ions.

HOWEVER,

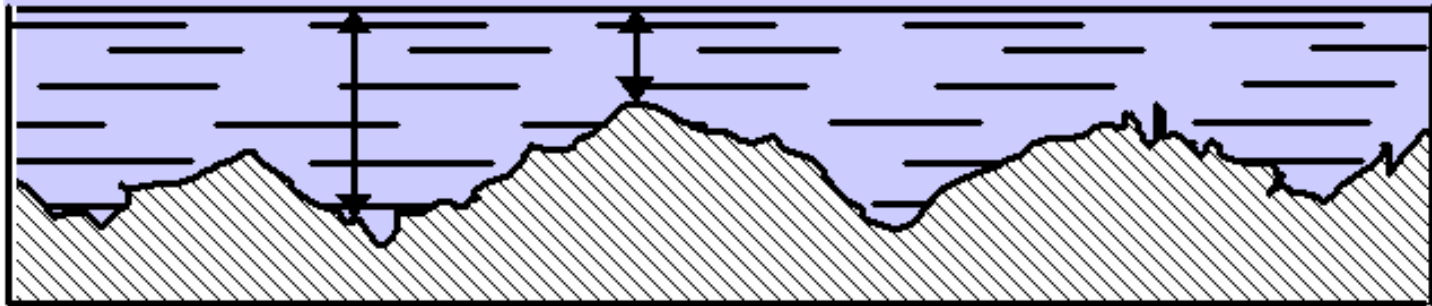
the presence of a viscous, high-resistivity film on the anode surface (as in the case of Cu EP in H_3PO_4)

is not in all cases essential for high quality polishing

Moreover, Jacquet and Elmore theories :

- do not answer to the question of metal oxidation during EP,
- do not explain the anodic polarization curves, i.e.,
- do not reveal the mechanism of anodic polishing, since they are mainly based on the influence of single factors.

According to Baumann and Ginsberg :



Jacquet model **does not apply** in case of:

- both vigorous agitation of the electrolyte
- voltages much higher than the *plateau* .

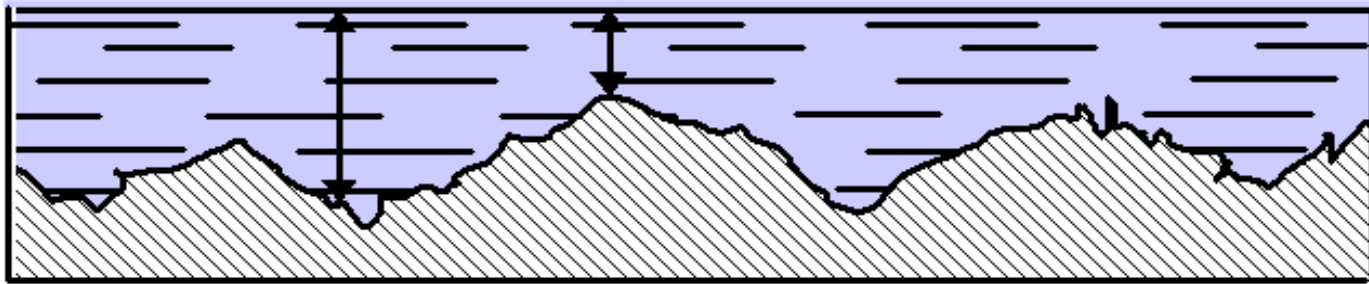
Electric field intensity is higher at edges and protuberances than at wells, cavities and craters.

Surface levelling occurs due to

GREATER DISSOLUTION PROBABILITY OF PEAKS .

Baumann F., Ginsberg H., Aluminium (BRD),32,11,706 (1956)

Elmore's model was criticized by Edwards :



Edward assumed that electropolishing processes are governed by **the diffusion of acceptors** as $(\text{H}_2\text{PO}_4)^-$, $(\text{HPO}_4)^{--}$, and $(\text{PO}_4)^{---}$ to the anode surface

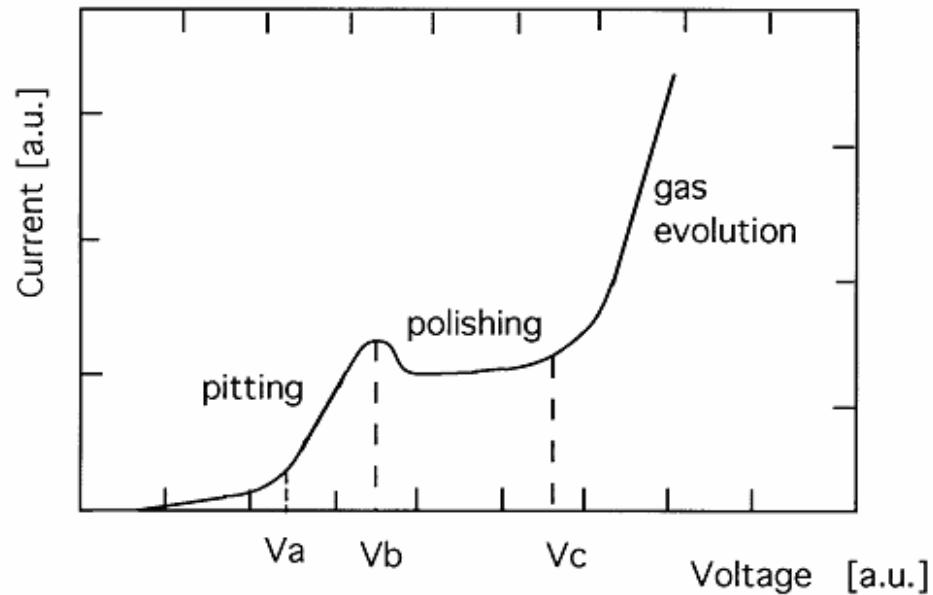
The polishing rate is **determined by the mobility of the acceptor toward the anode**

The acceptor concentration gradient is higher on peaks rather in valleys

Edwards J., J. Electrochem Soc., 100, n.7, 189c (1953)

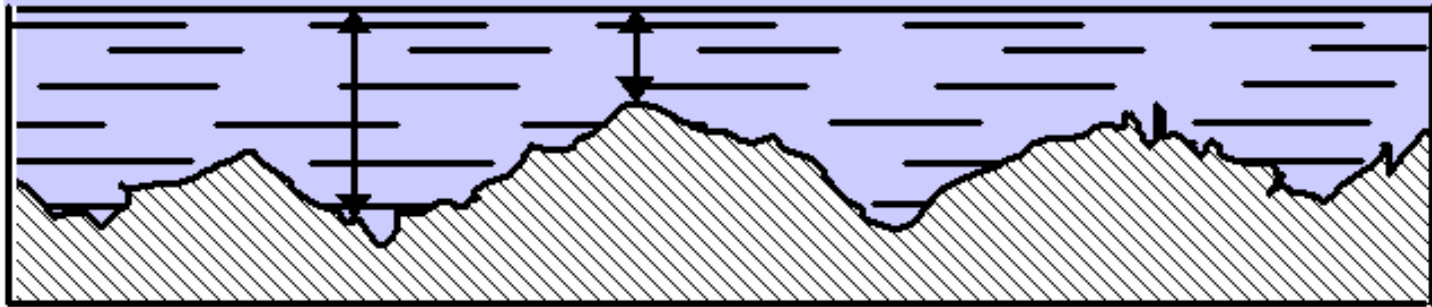
Edwards explains the plateau:

the current remains constant until V_c , i.e. until reaching the potential corresponding to the discharge of hydroxyl ions



since over this range the current is determined by the rate of supply of acceptor ions to the anode surface.

According to Vozdvizhenskii :

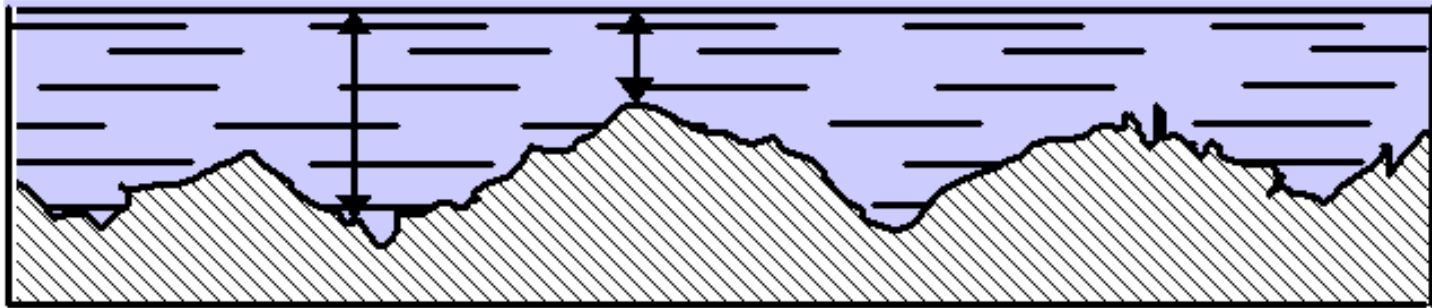


The anodic dissolution is a "reversed electrolytic crystallization", which depends on the metal texture.

Mechanical working of metals produces a micro-rough surface with deformed crystal sites, preferentially dissolved upon metal anodic polarization.

EP causes leveling of the initial roughness, but also leads to the appearance of a new surface roughness due to anodic etching.

Vozdvizhenskii's model is considered incomplete by Shigolev :

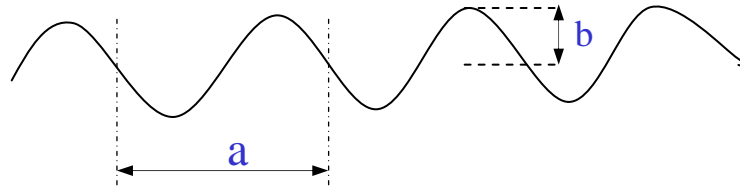


under optimum polishing conditions,
the metal surface layer can be dissolved
uniformly regardless of surface texture

Wagner theory of electropolishing:

(The first quantitative mathematical description of the process)

Surface roughness is described by a sine-wave profile with a wavelength, **a**, and an amplitude, **b**;



The displacement **u** for a decrease from **b₀** (at time $t = 0$) to **b** (time t) is given by:

$$\mathbf{u} = \mathbf{a}/2\pi \cdot \ln \mathbf{b}_0/\mathbf{b} \quad \text{for } \mathbf{b} \ll \mathbf{a}, \mathbf{a} \ll \delta$$

C. Wagner, J. Electrochem. Soc., 101, 225 (1954)

The theory predicts a linear plot

for $\Delta m/A$ vs $\ln b_0/b$

finding good agreement with experimental results

From that one calculates the metal loss per unit area, $\Delta m/A$ and the charge consumed, Q

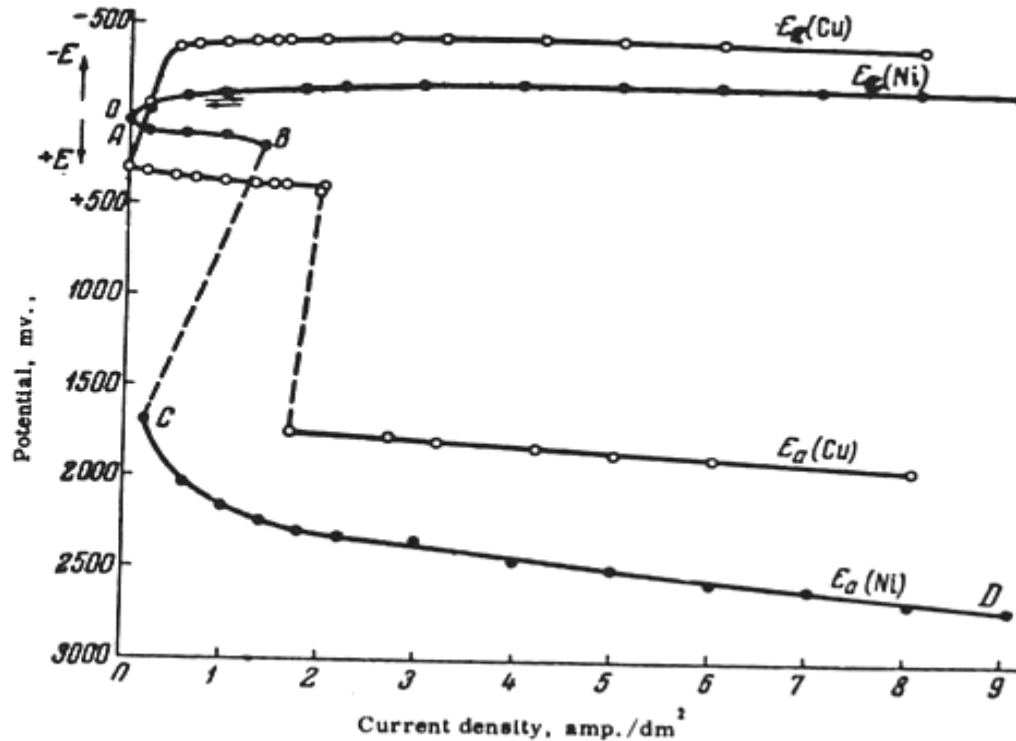
Many authors believe that EP is accompanied by the formation of **passive films on the anode**

Current Electrochemistry
accurately explains the EP
process on the basis
of the modern concepts of
anodic passivity of metals

During the process the metal
does not assume a steady stable
passivation state,
because of chemical dissolution of a
passivating oxide film in the electrolyte

Surface leveling takes place because
the passivation of wells is more stable
and it inhibits etching
Peaks are instead dissolved more rapidly

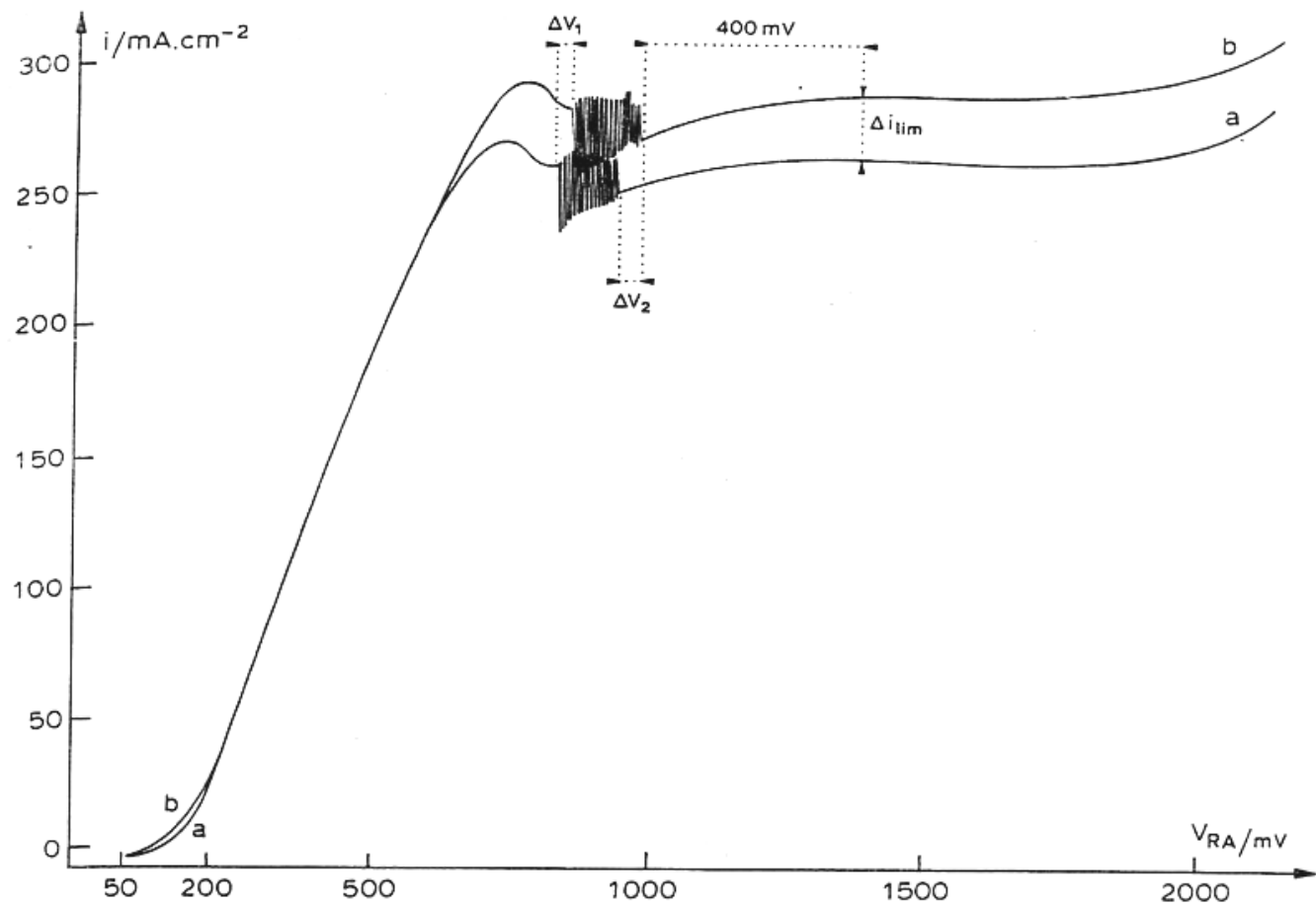
Anodic polarization curves are quite similar to curves obtained in the case of anodic passivation processes



Anodic and Cathodic polarization curves for Ni in H_2SO_4 at 40° and Cu in H_3PO_4 at 20°

Plotting of Polarization Curves

- Comparison of **log-*i*** and **linear-*i*** plots
- Identification of **anodic** and **cathodic** regions on log-*i* plots
- Orientation of plots



Systemes Electrochimiques Autooscillants

P.Poncet, M. Braizaz, B. Pointu, J. Rousseau

Journal de chimie Physique, 1977, 74 n.4

Systeme Cu/H₃PO₄: Instabilité et Oscillations

P.Poncet, M. Braizaz, B. Pointu, J. Rousseau

Journal de chimie Physique, 1978, 75 n.3

Photoeffects on the Cu/H₃PO₄ interface

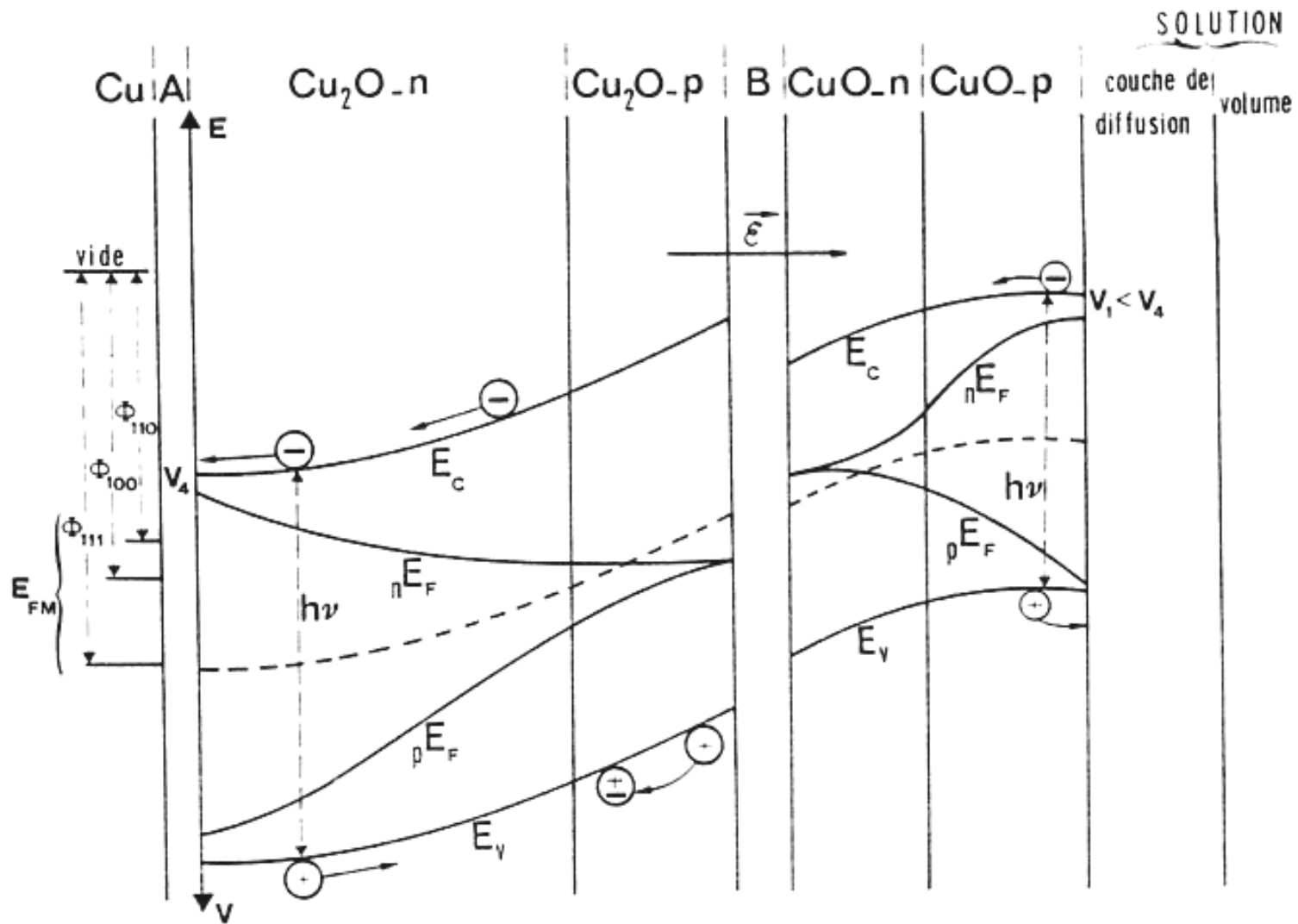
P.Poncet, M. Braizaz, B.Pointu, J. Rousseau, N. Muhlstein

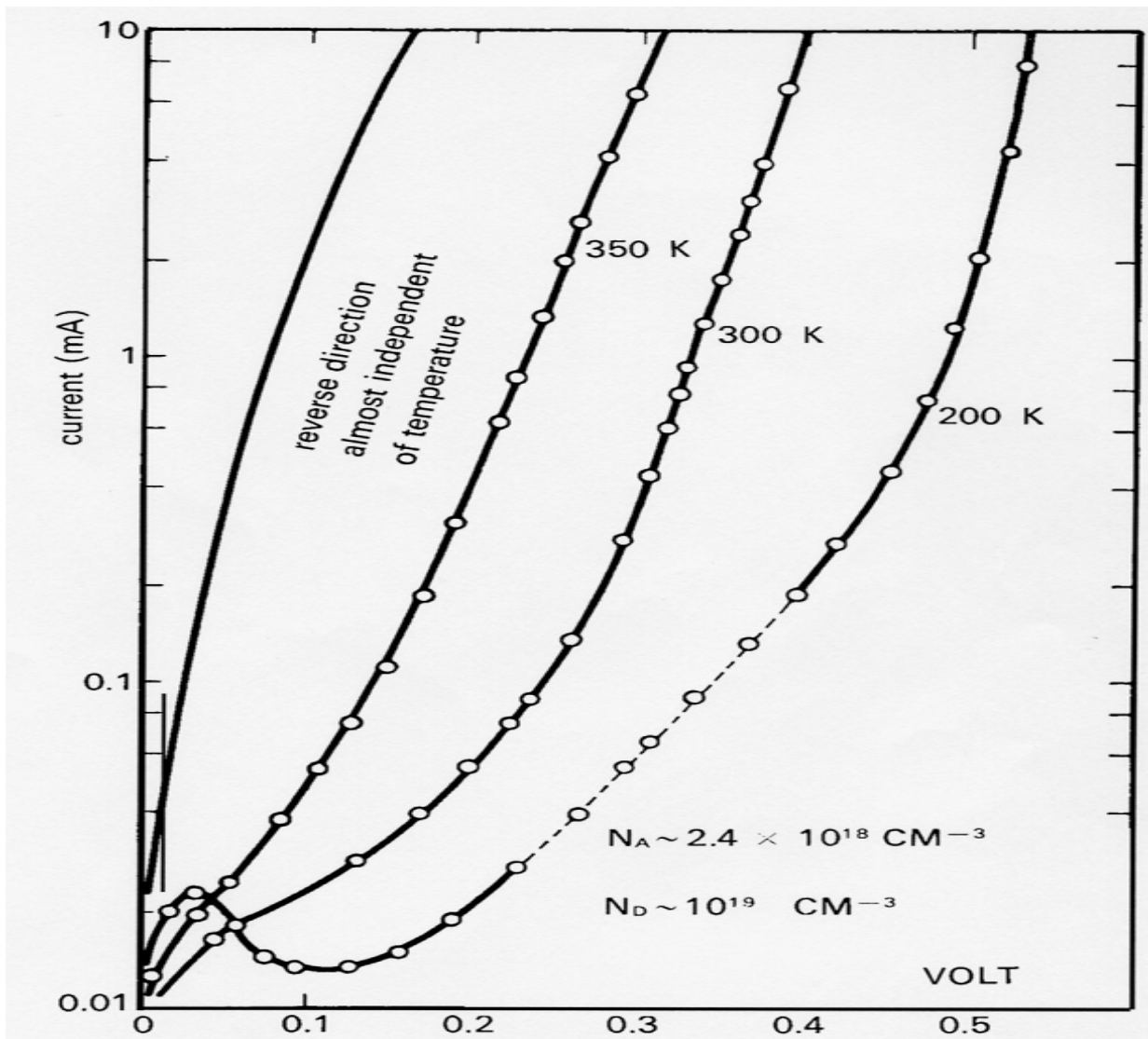
Journal Electroanal. Chem, 122 (1981), 111

Photocourants obtenus sur des anodes de cuivre monocristallin

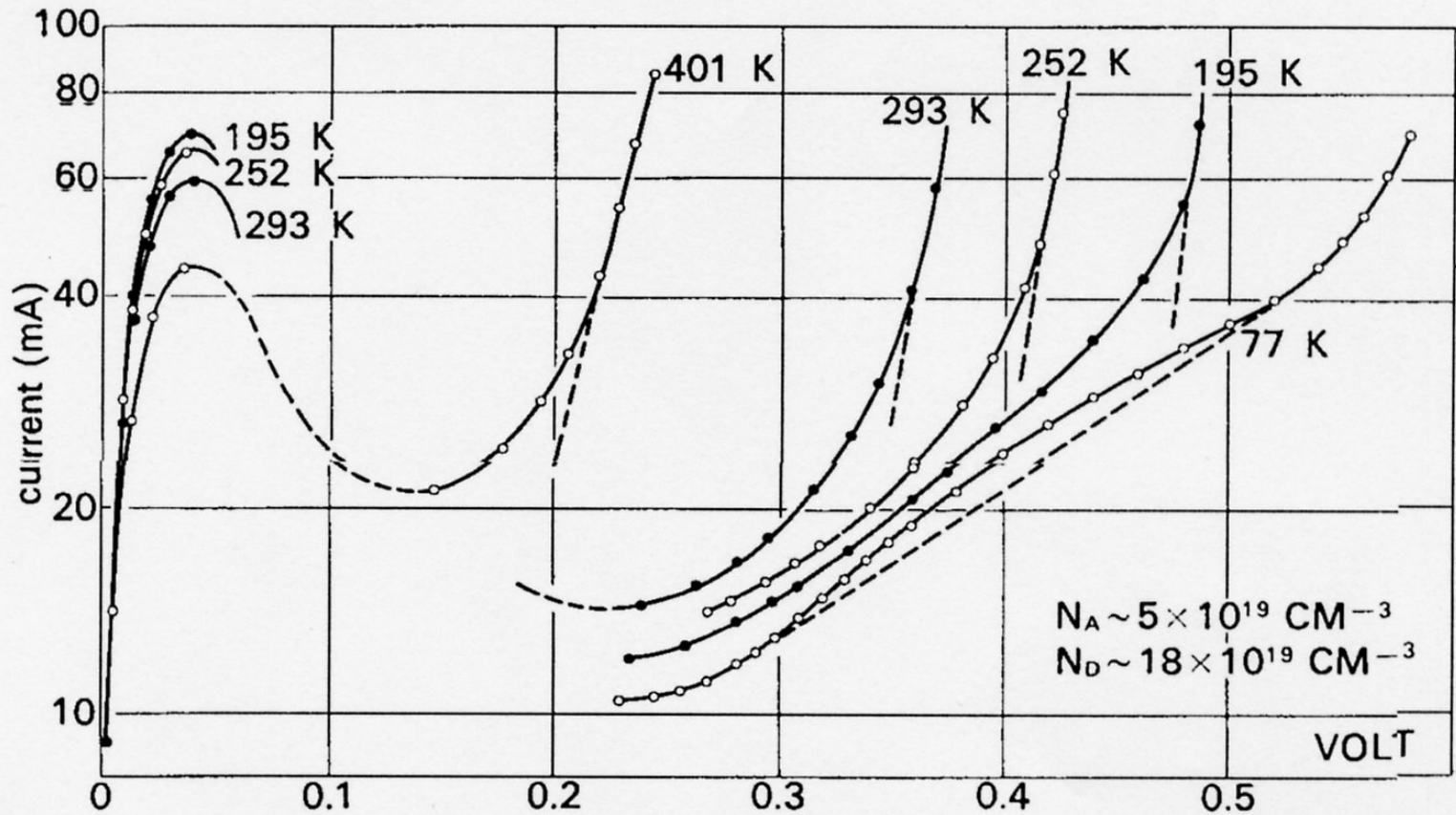
B. Pointu, P. Poncet

Thin solid films, 79 (1981) 125





Semilog plot of I-V characteristics of a tunnel diode



Semilog plots of current-voltage characteristics in a tunnel diode, where $N_A \sim 5 \times 10^{19} \text{ cm}^{-3}$ and $N_D \sim 1.8 \times 10^{19} \text{ cm}^{-3}$.

The search for new electrolytes:

Acids less aggressive and more easy to handle,

Lower costs both when purchasing and when exhausting

Higher throwing power

Effect of process parameters on the plateau

Temperature:

The temperature does not affect the plateau voltage range, but only the current density

Concentration:

Ibid., Plateau range unchanged, current density increases

Viscosity:

Current density inversely proportional to Viscosity

Stirring:

It increase almost linearly the current density

The method of voltage choice by locking to the minimum of differential conductance, allows to **automatically find always the best EP conditions**

You can correlate the minimum conductivity of the electrolyte versus the acid/moderator percentage, and in such a way find new electrolytes

Example:

a new electrolyte for Nb

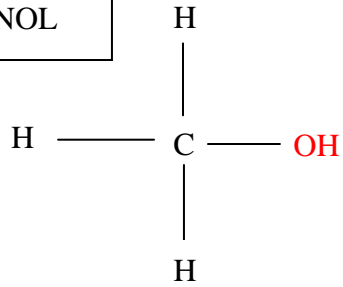
HF + OXALIC ACID + BORIC ACID + H₃PO₄

30% HF, 15% H₃PO₄, 30 gr/l Oxalic acid, 10 gr/l Boric acid

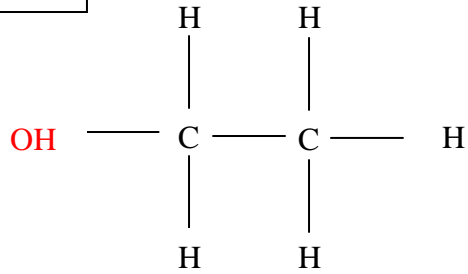
(Palmieri et al., Tsukuba SRF Workshop 2001)

Monols

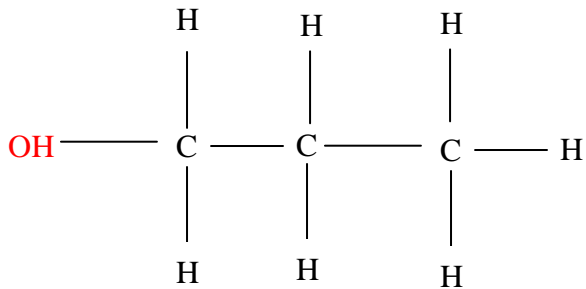
METHANOL



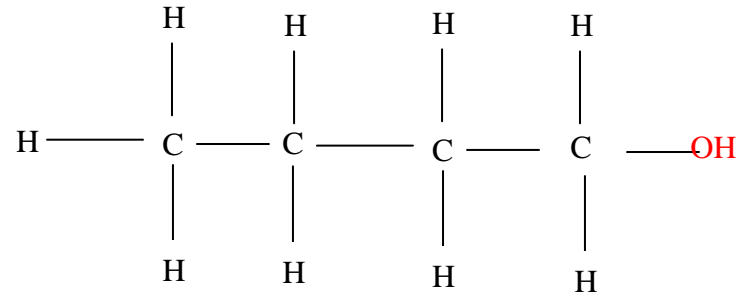
ETHANOL



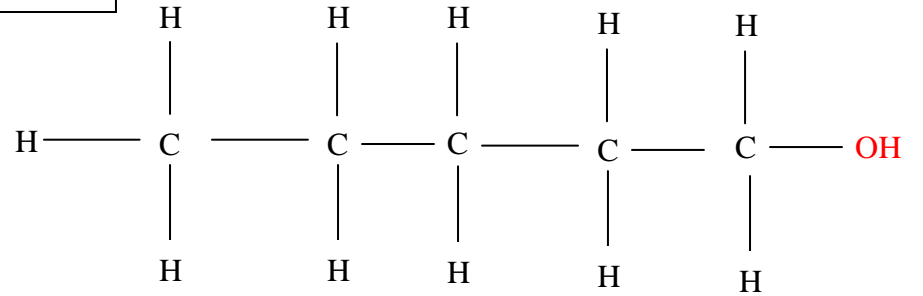
1-PROPANOL



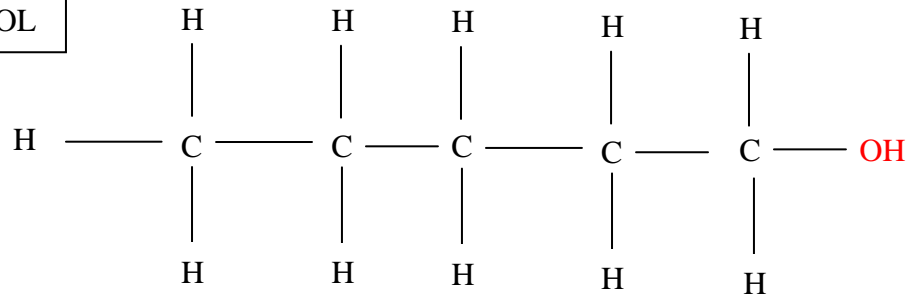
1-Butanol



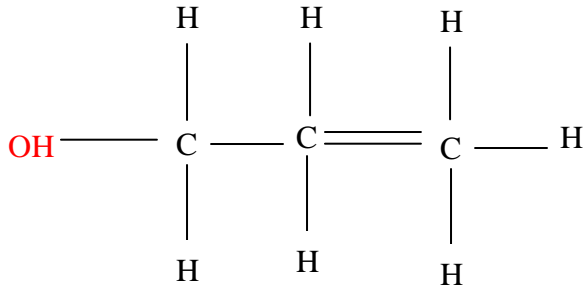
1-PENTANOL



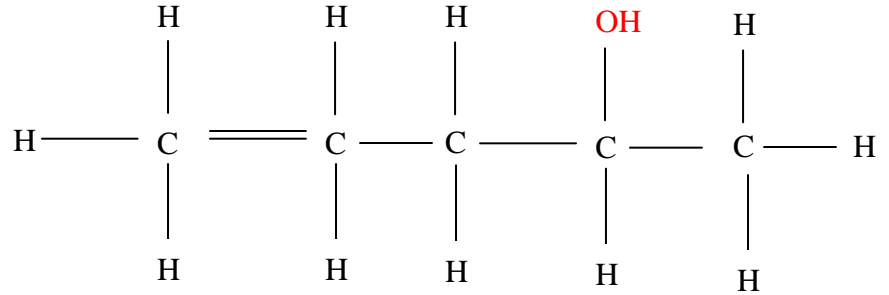
1-HEXANOL



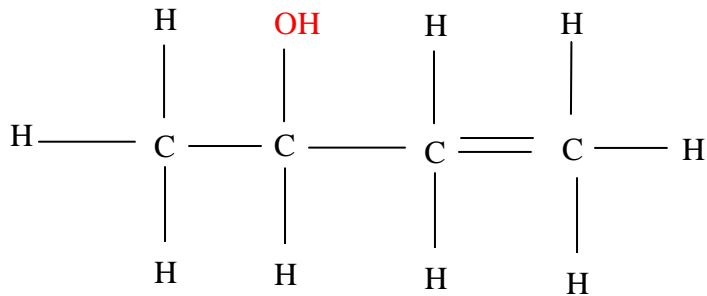
2-Propen-1-ol



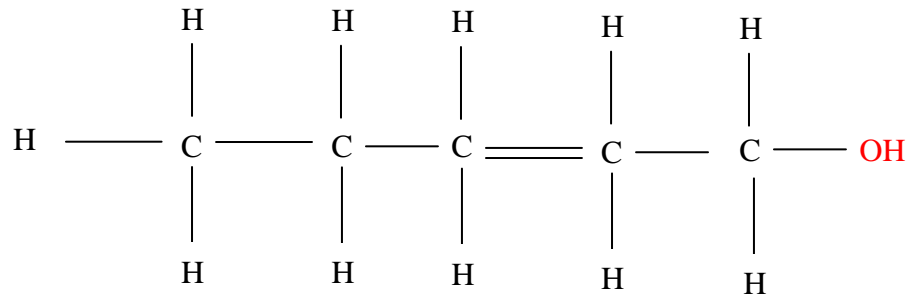
4-Penten-2-ol



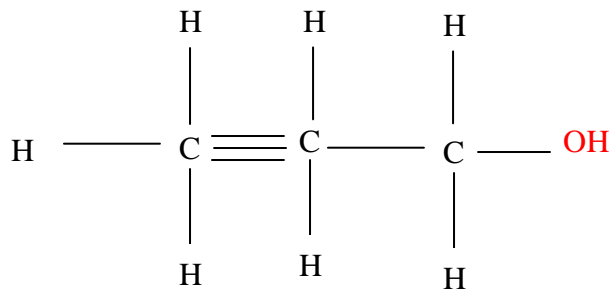
3-Buten-2-ol



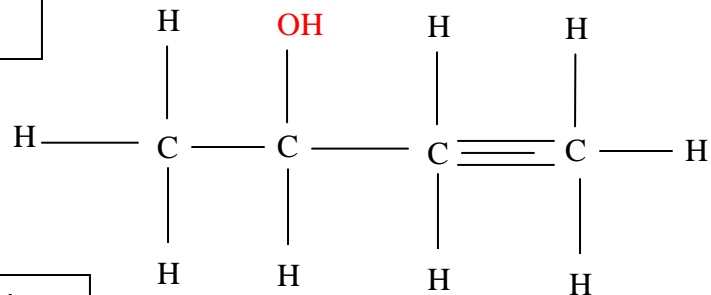
2-Hexen-1-ol



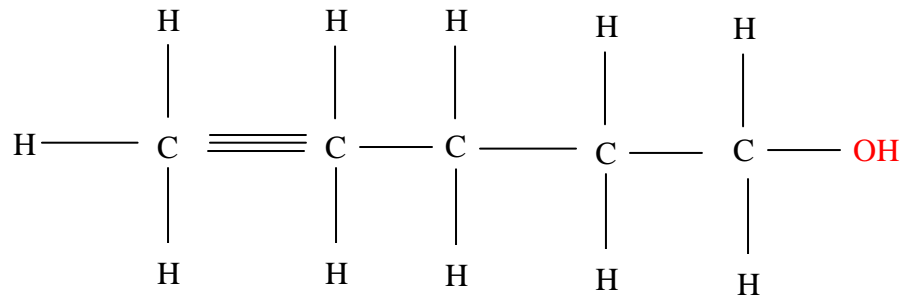
2-Propyn-1-ol



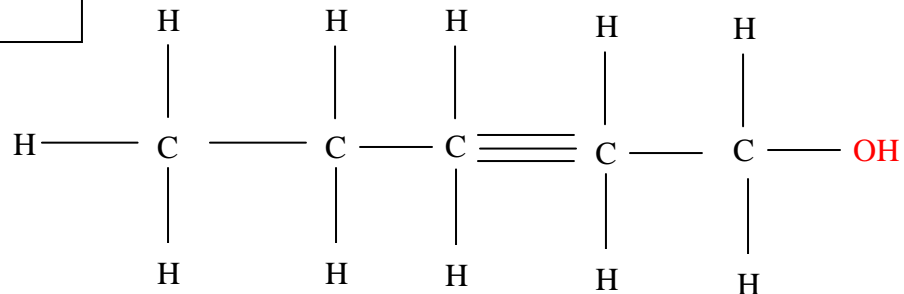
3BUTIN-2OL



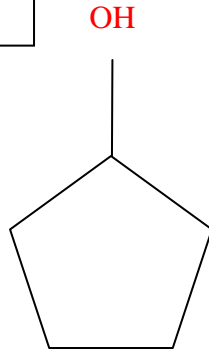
4-Pentyn-1-ol



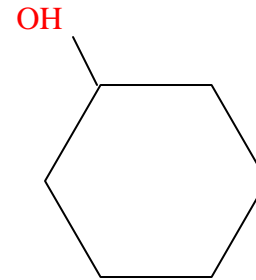
2-HEXIN-1OL



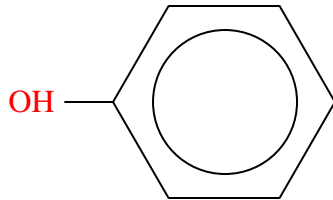
Cyclopentanol



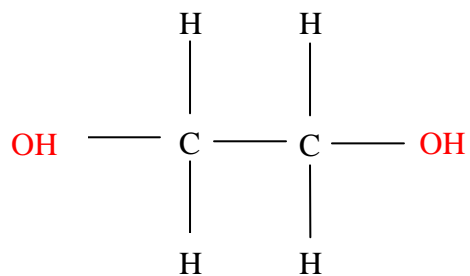
Cyclohexanol



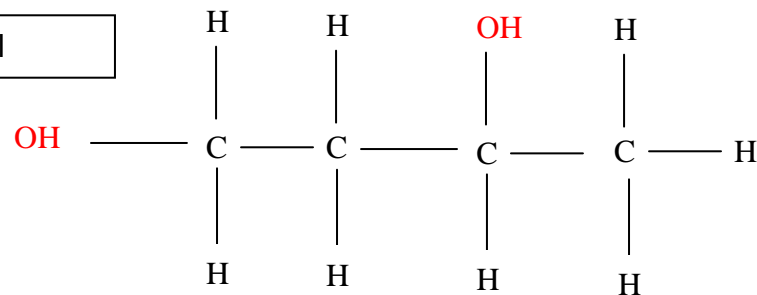
Phenol



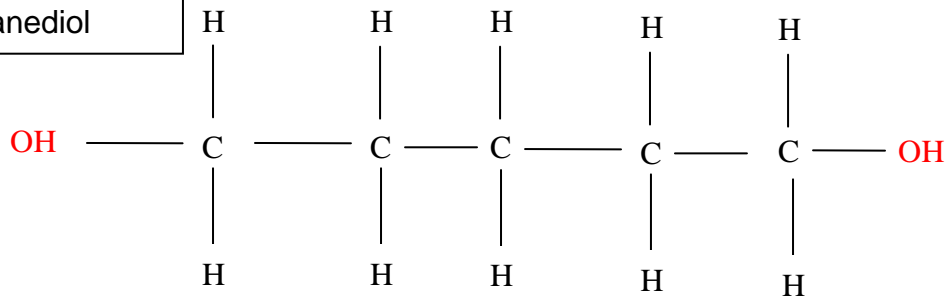
1,2-Ethandiol



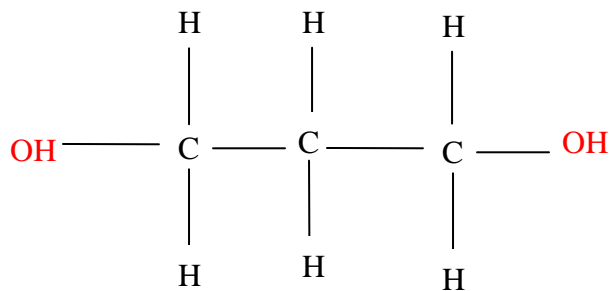
1,3-Butanediol



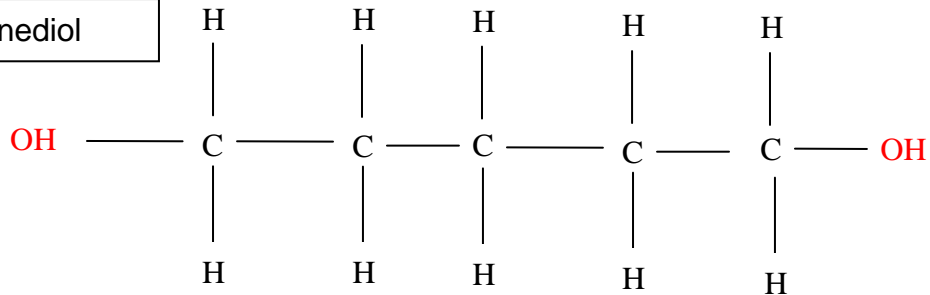
1,5-Pentanediol



1,3-Propanediol

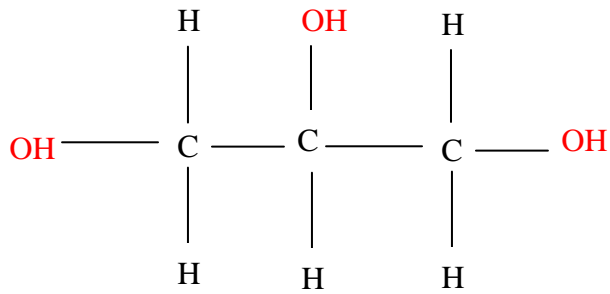


1,6-Hexanediol

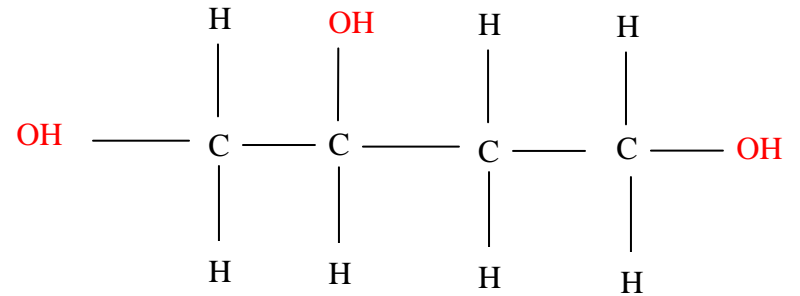


TRIOL

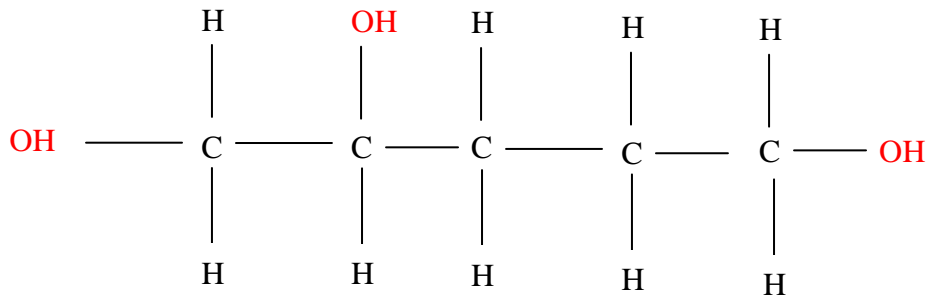
GLYCEROL



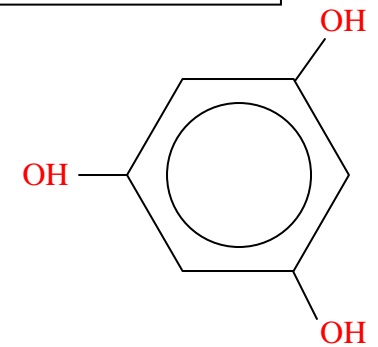
1,2,4 -BUTANETRIOL



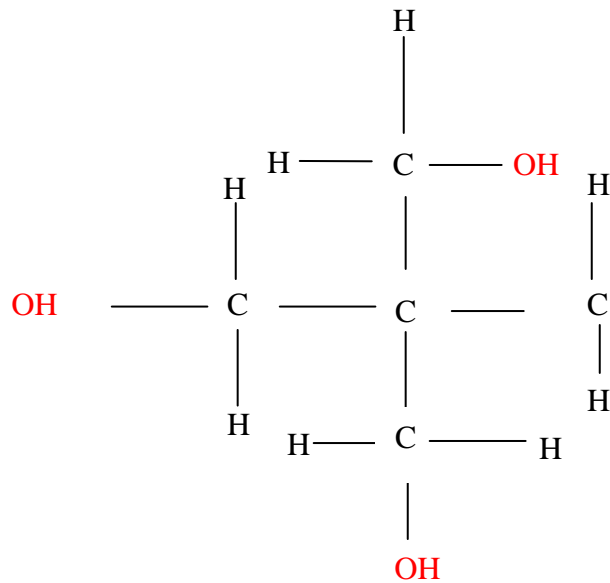
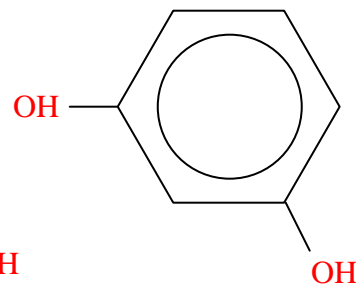
1,2,6 -HEXANTRIOL



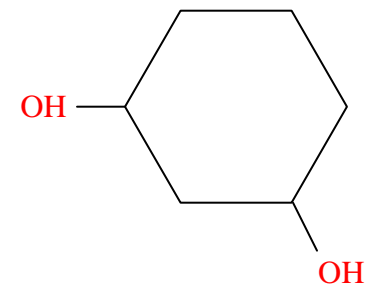
1,3,5-TRIHydroxybenzene
(TMB)



1,4-BENZENEDIOL



TETRAKIS(HYDROXYMETHYL)METHANE
PENTAERYTHRITOL



1,3-CYCLOHEXANEDIOL

A well known hydrogen free electrolyte for Nb:

An electrolyte for Nb was introduced by Schober and Sorajic, extrapolating what proposed by Epelboin [Rev. Met. **49** (1952) 863.]

The electrolyte is 0.05 mole/liter $\text{Mg}(\text{ClO}_4)_2$ in CH_3OH
EP Voltage is 50-70 V, bath temperature -5°C

Since the electrolyte does not contain a hydrogen radical, no intake of hydrogen is possible

Perchloric acid has been largely used as constituent of electropolishing baths for its peculiar properties,

for its easy dissolution in non aqueous media,

for its powerful dissolution action of metals and alloys

for the remarkable solubility of numerous metallic perchlorates in acid milieu

However, in the technique literature, many explosions caused by perchloric acid solutions have been brought to notice

Polishing baths perchloric acid-based can be divided into two main classes:

Strong solutions, containing perchloric acid mixed with anhydride or with acetic acid

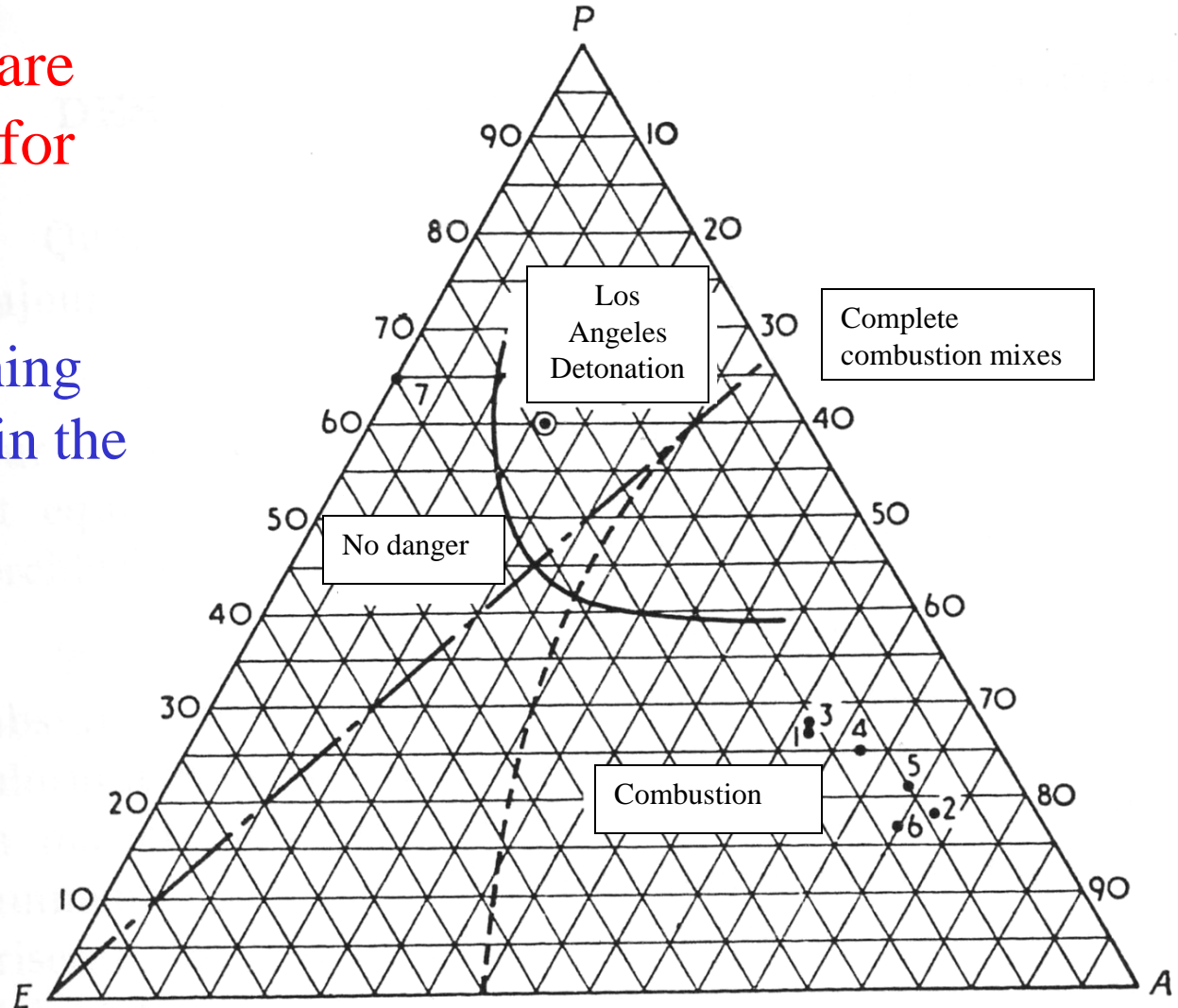
Less concentrated solutions containing perchloric acid mixed with ethylic acid, acetic acid or acetic anhydride

Notice!!!!!! Some authors maintains that ethyl perchlorate is as dangerous as Nitroglycerin

Mixes containing less than 55% in weight of perchloric acid cannot explode

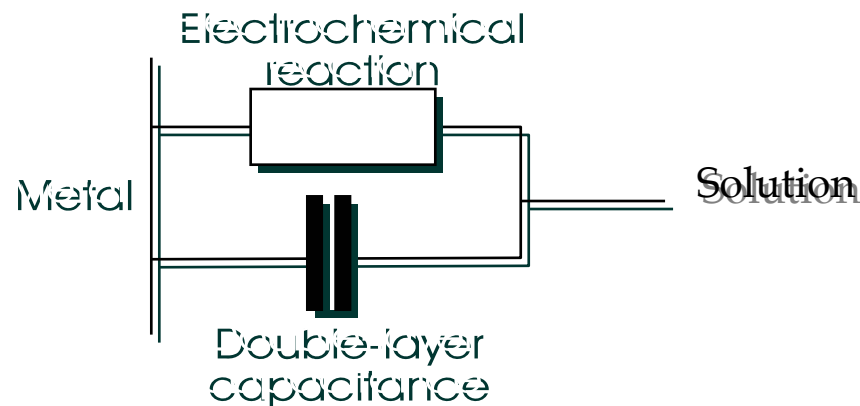
Unfortunately they are the less interesting for the EP use

The convenient polishing baths are just located in the flammable field

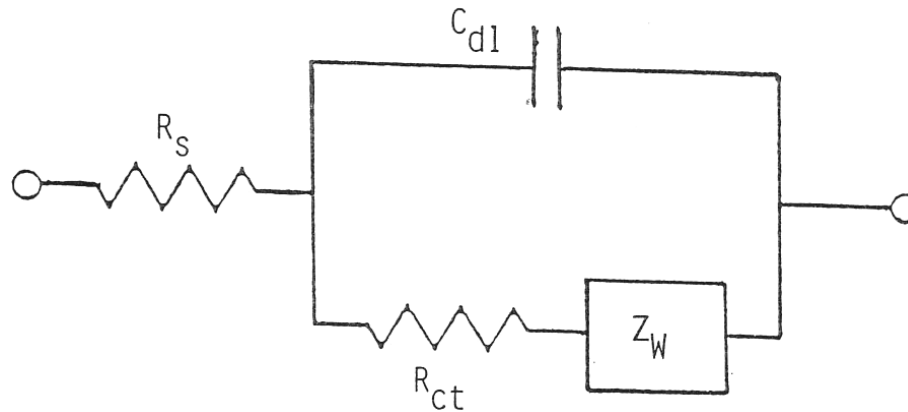
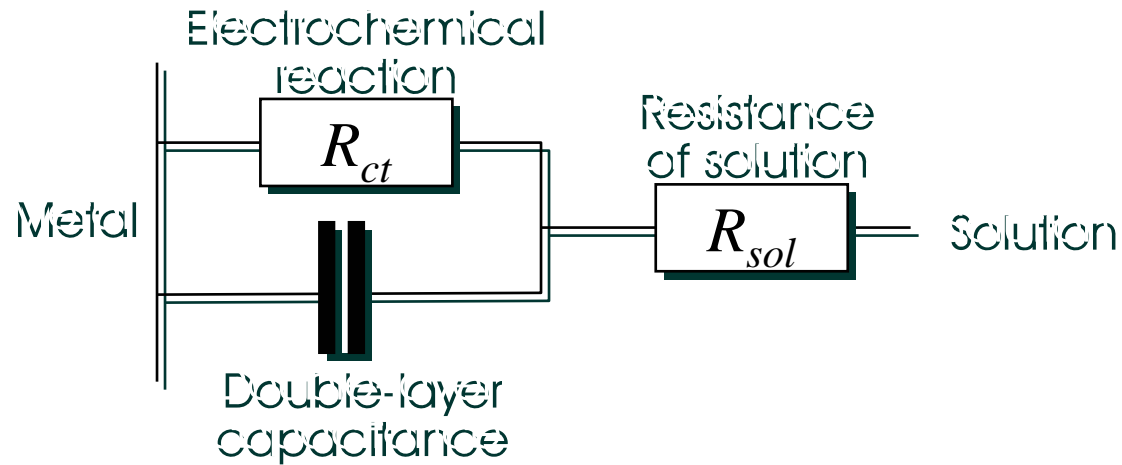


Equivalent Circuits

- An electrical circuit with the same properties as a metal-solution interface
- The simplest circuit is a resistor, R_{ct} , corresponding to the polarization resistance, in parallel with a capacitor, C_{dl} , corresponding to the double layer capacitance

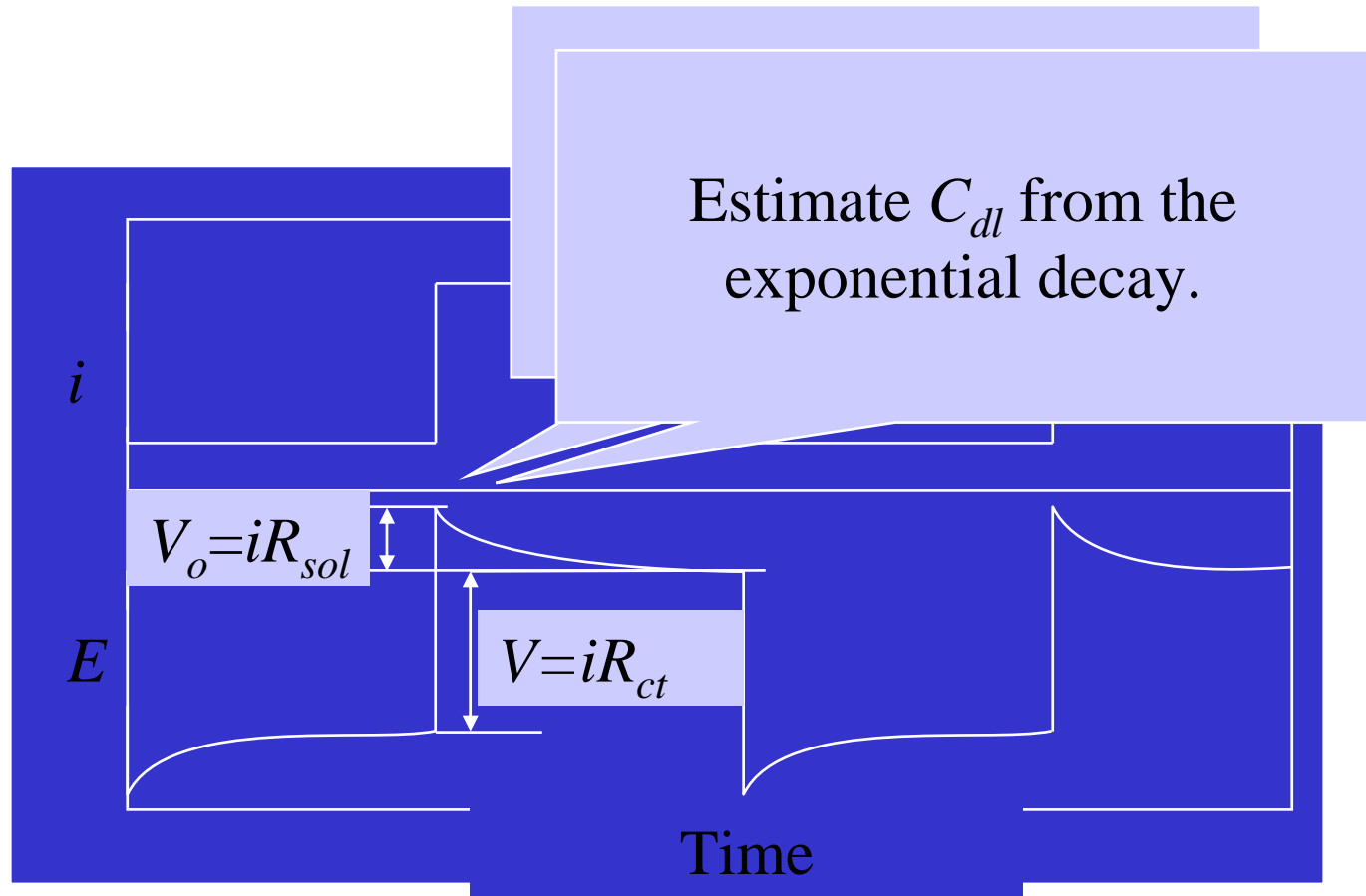


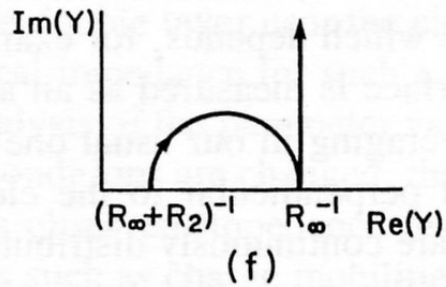
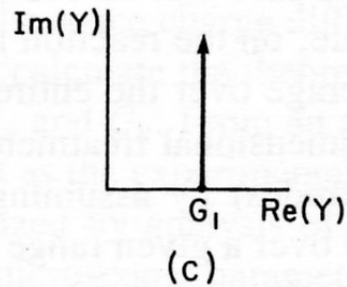
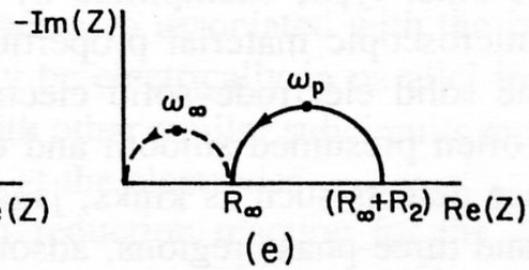
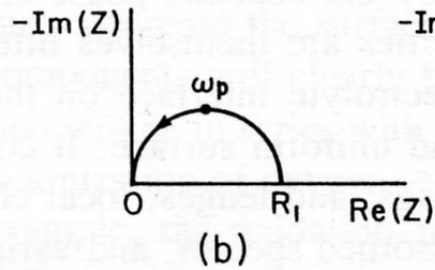
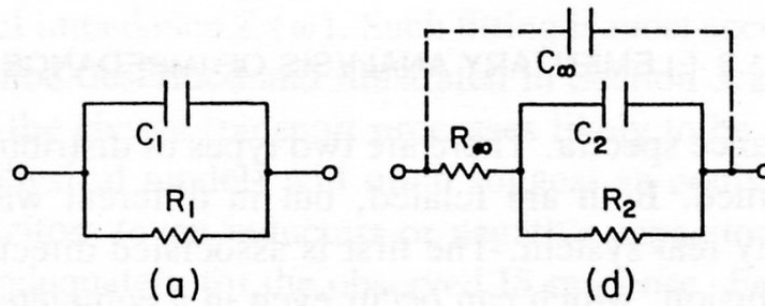
❖ The Randles equivalent circuit adds a series resistor, corresponding to the solution resistance



Analysis of Solution Resistance

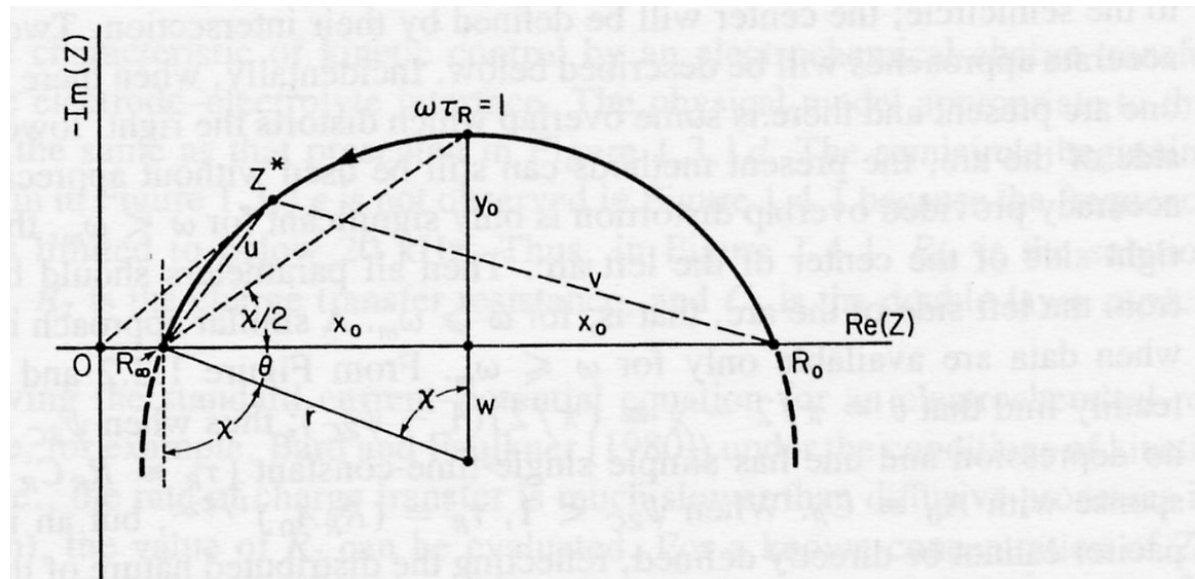
we can estimate R_{sol} , C_{dl} and R_{ct}





Figures 1a and d show two common RC circuits. Parts b and e show their impedance plane plots and c and f their admittance plane plots. Arrows indicate the direction of increasing frequency.

By impedance measurements, one can distinguish electromigration through the passive layer from diffusional transport



And it is definitely the most powerful method
for investigating electrolytic cells

THE END