# Corosion, Passivity and Metallurgy

*by*

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- **Introduction to the aqueous corrosion of metals and alloys**
- **Passivity and Passive films**
- **Passivity breakdown**
- **Metallurgical effects**

# Part I: Introduction to the aqueous corrosion of metals and alloys

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Corrosion is an irreversible phenomenon which results from the basic thermodynamic characteristics of the materials and the nature of their environment. In this lecture we will look at the water corrosion phenomena applicable to metals and alloys, but excluding both high temperature oxidation phenomena and corrosion of non-metallic materials

# Experimental Evidences

- **Formation of rust and other corrosion products**

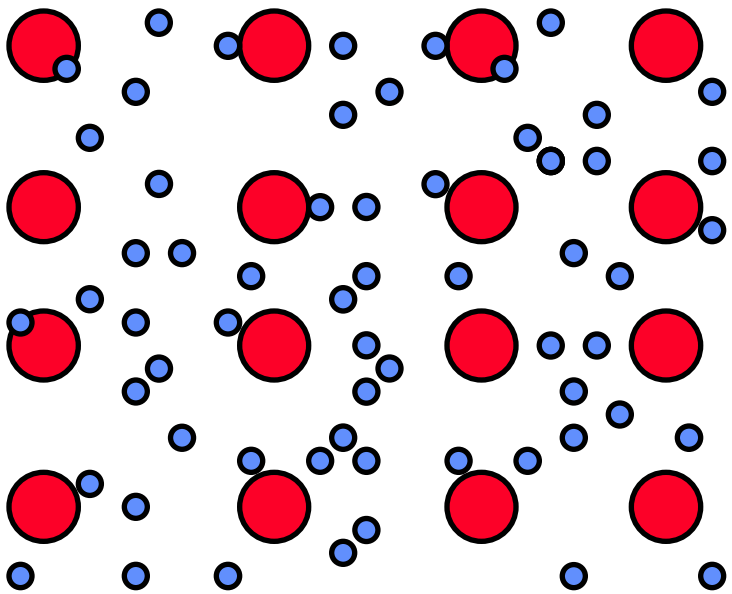

**Metallurgical effects**

- **Electrochemical (anodic) dissolution**

$$M \rightarrow M^{++} + 2e^{-}$$

**⇒ loss of weight and pollution…**

# What is a metal ?



A metal is an assembly of cations (positive) arranged in a lattice structure immersed in a gas of delocalized electrons (negative) which ensure the cohesion of the structure.

**A metal is a reservoir of electrons.**
**Consequences:**

1) A metal is a good conductor of electricity and heat.

2) The electron gas reflects light waves $\Rightarrow$ optical properties

3) A metal is ductile (dislocations easy to displace)

4) A metal is oxidizable (easy separation of cations and electrons).

# The oxidation of metals

*(example of a divalent metal)*

**Dry oxidation**

$$\boxed{M + \frac{1}{2}O_2 \rightarrow MO} \quad \begin{cases} M \rightarrow M^{++} + 2e^- \\ \frac{1}{2}O_2 + 2e^- \rightarrow O^{--} \\ M^{++} + O^{--} \rightarrow MO \end{cases}$$

**Water passivation**

$$\boxed{M + H_2O \rightarrow MO + 2H^+ + 2e^-}$$

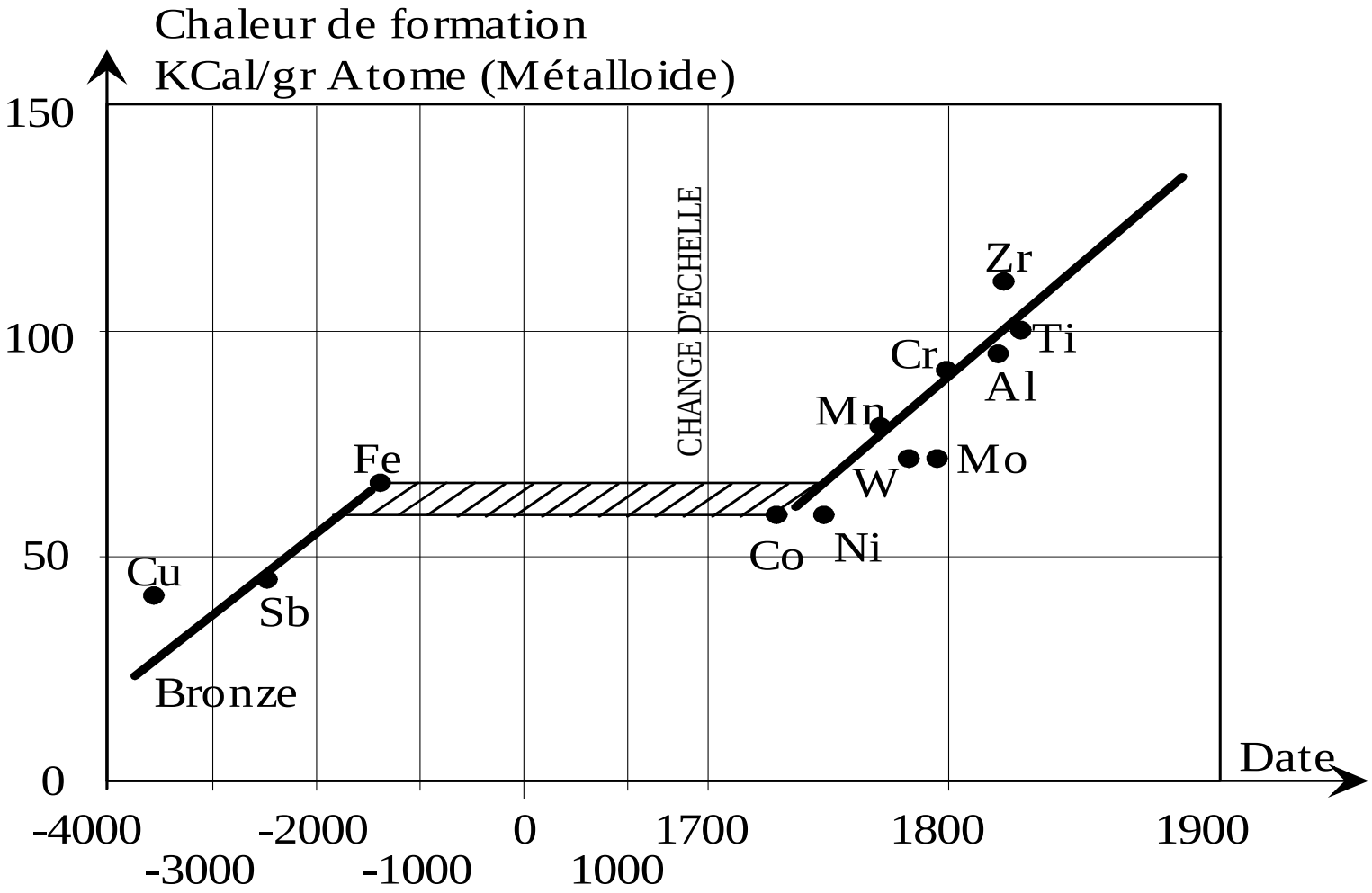
**Water dissolution**

$$\boxed{M + nH_2O \rightarrow M^{++}(H_2O)_n + 2e^-}$$

**Precipitation of an oxide or a hydroxide (rust)**

$$\begin{cases} M^{++} + H_2O \rightarrow \underline{MO} + 2H^+ \\ \text{ou} \\ M^{++} + 2H_2O \rightarrow M(\underline{OH})_2 + 2H^+ \end{cases}$$

# Consequences on the history of metallurgy



# Consequences on the Corrosion resistance :
## The Paradox of passivity

**The more oxidisable materials can protect themselves by the formation of their own layer of corrosion in the form of a very thin protective film (called a passive film).**

**For these materials, the question of corrosion resistance no longer arises in terms of rate of dissolution, but in terms of the stability of the protective oxide.**

**These materials are described as "stainless", quite simply (but this paradox is only apparent) because their oxidation is fast enough and intense enough to inhibit any subsequent corrosion.**

**Example: the Corrosion resistance of S.S. results from their Chromium content (more than 12%)**

## The predominant role of water in Corrosion processes

**The oxygen in the iron oxides is drawn essentially from the molecules of water and not at all or only very slightly from the oxygen in the air, as is most often thought (the oxygen only encourages the cathodic reaction as will be explained later).**

**In temperate climates, atmospheric corrosion may be considered a water corrosion phenomenon due to the presence of a film of water on the surface of the metal which generally constitutes a cold surface encouraging the formation of condensation.**

# Oxydoreduction of water

**Oxidation:** $H_20 \rightarrow 2\ H^+ + ½\ O_2 + 2\ e^-$

(oxygen evolution reaction)

**Reduction:** $H_20 + e^- \rightarrow OH^- + ½\ H_2$

(hydrogen evolution reaction)

## Other instances of oxido-reductive processes

$$4OH^- \leftrightarrow 2H_2O + O_2 + 4e^-$$ *and* $$2H_3O^+ + 2e^- \leftrightarrow 2H_2O + H_2$$

$$NO_3^- \rightarrow NO_2 + \frac{1}{2}O_2 + e^-$$ , $$Fe^{+++} + e^- \rightarrow Fe^{++}$$

**Etc…**

# The Bronsted Acidobasicity of Water

**Water is a Bronsted amphoter**

**Bronsted acids***

$H_2O \rightarrow \mathbf{H^+} + \mathit{OH^-}$

$\mathbf{H_3O^+} \rightarrow H_2O + \mathbf{H^+}$

**Bronsted bases***

$H_2O + \mathbf{H^+} \rightarrow \mathit{H_3O^+}$

$\mathbf{OH^-} + \mathbf{H^+} \rightarrow H_2O$

**Acid-base balance**

$\mathbf{2H_2O \leftrightarrow H_3O^+ + OH^-}$

$H_3O^+$ = hydronium ion
= protonated water
(or hydrated proton)

$OH^-$ = hydroxyl ion
= deprotonated water

*(*Conjugated acids and bases are indicated in italics)*

# Dissociation of water on metal surfaces

## (Bronsted acidobasicity)

| Metal | Solution |
|---|---|
| Acid | $(OH_2)$ + $\{H_2O\}$ |
| | ↓ |
| Base | $(OH^-)$ + $\{H_3O^+\}$ |
| Base | $(H_2O)$ |
| | ↓ |
| Acid | $(H^+)$ + $\{OH^-\}$ |

$$(OH^-)_{ad} + H^+ \longleftrightarrow (H_2O)$$

$$(H^+)_{ad} \longleftrightarrow H^+$$

The consequences of water dissociation:

**(1) Adsorbed surface charge**

$$\sigma_{ad} = q[H^+_{ad} - OH^-_{ad}]$$

**(2) Potential drop**

at the metal/electolyte interface

$$V_H = \sigma_{ad}/C_H$$

## Formation de complexes hydratés

*(Acidobasicité de Lewis)*

**cation solvaté → cation hydraté**

$$(M^{++}, H_2O) \rightarrow (MOH_2)^{++}$$

## Hydrolyse des complexes hydratés

*(Acidobasicité de Bronsted)*

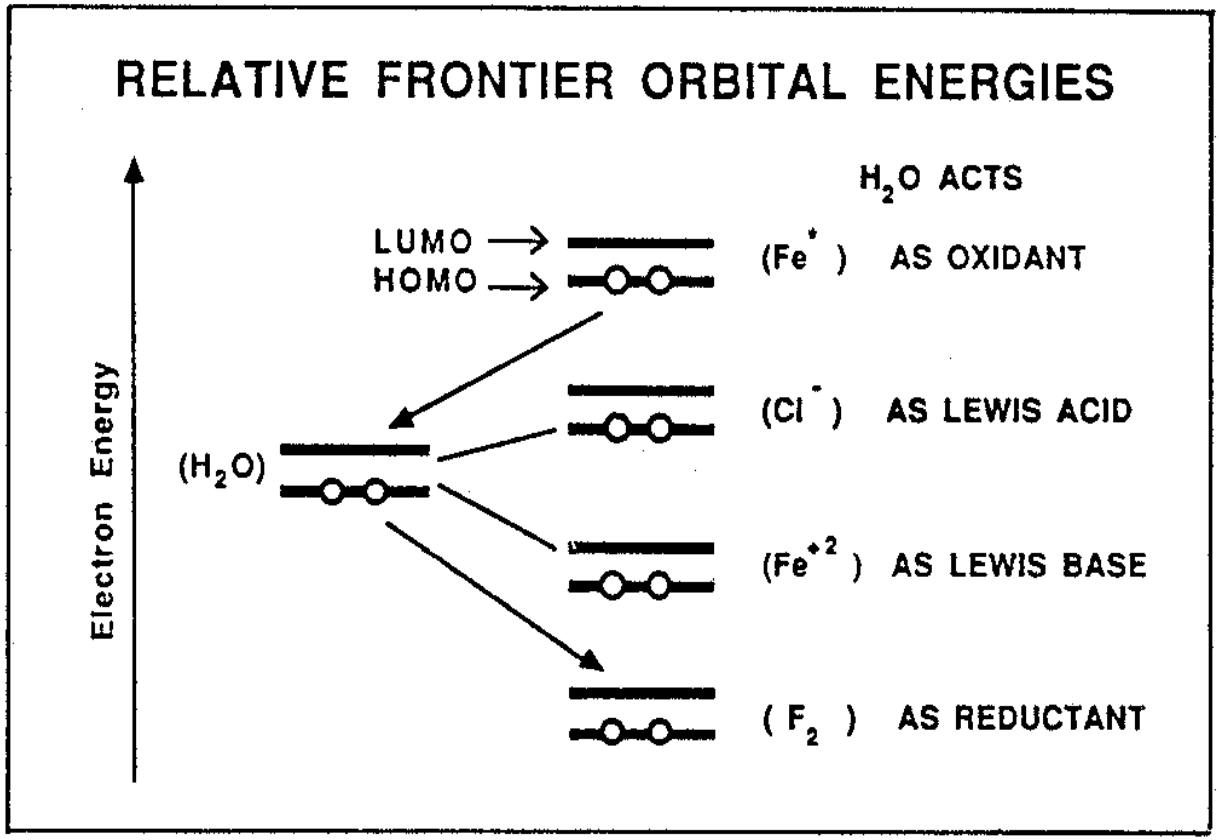
**Hydrolyse**

$$(MOH_2)^{++} \rightarrow MOH^{+} + H^{+}$$

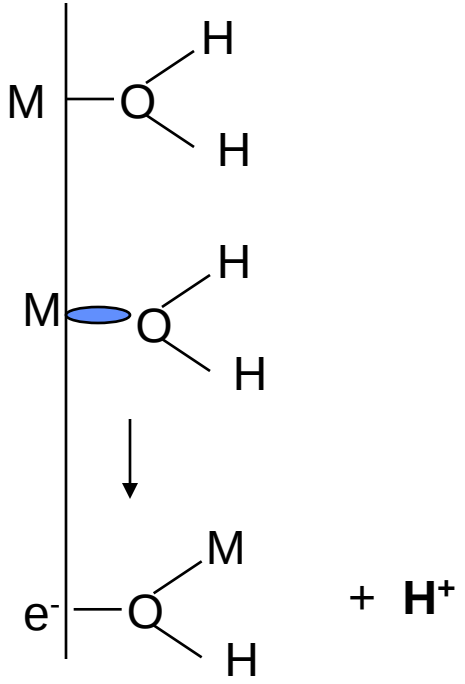
**Précipitation de l 'oxyde**

$$MOH^{+} \rightarrow MO + H^{+}$$

# Oxydoreduction and Lewis acidobasicity of water



# Metal water interactions
## The first steps




**Physisorption**

**Chemisorption**

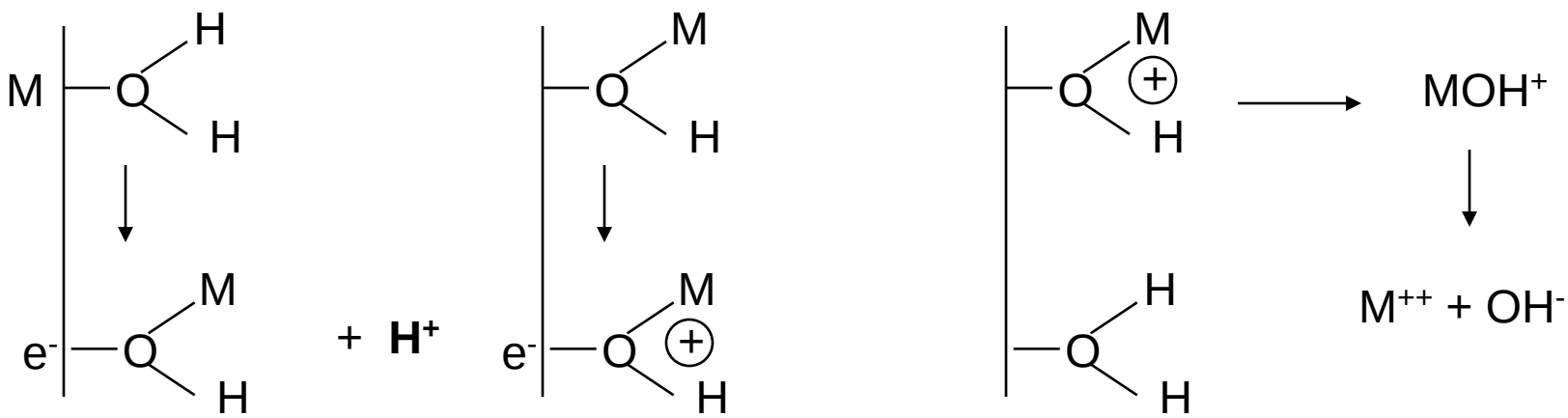
(Lewis reaction)

**Deprotonation**

(Bronsted reaction)

+ **Oxidation**

# Water corrosion




**Oxidation** **Dissolution**

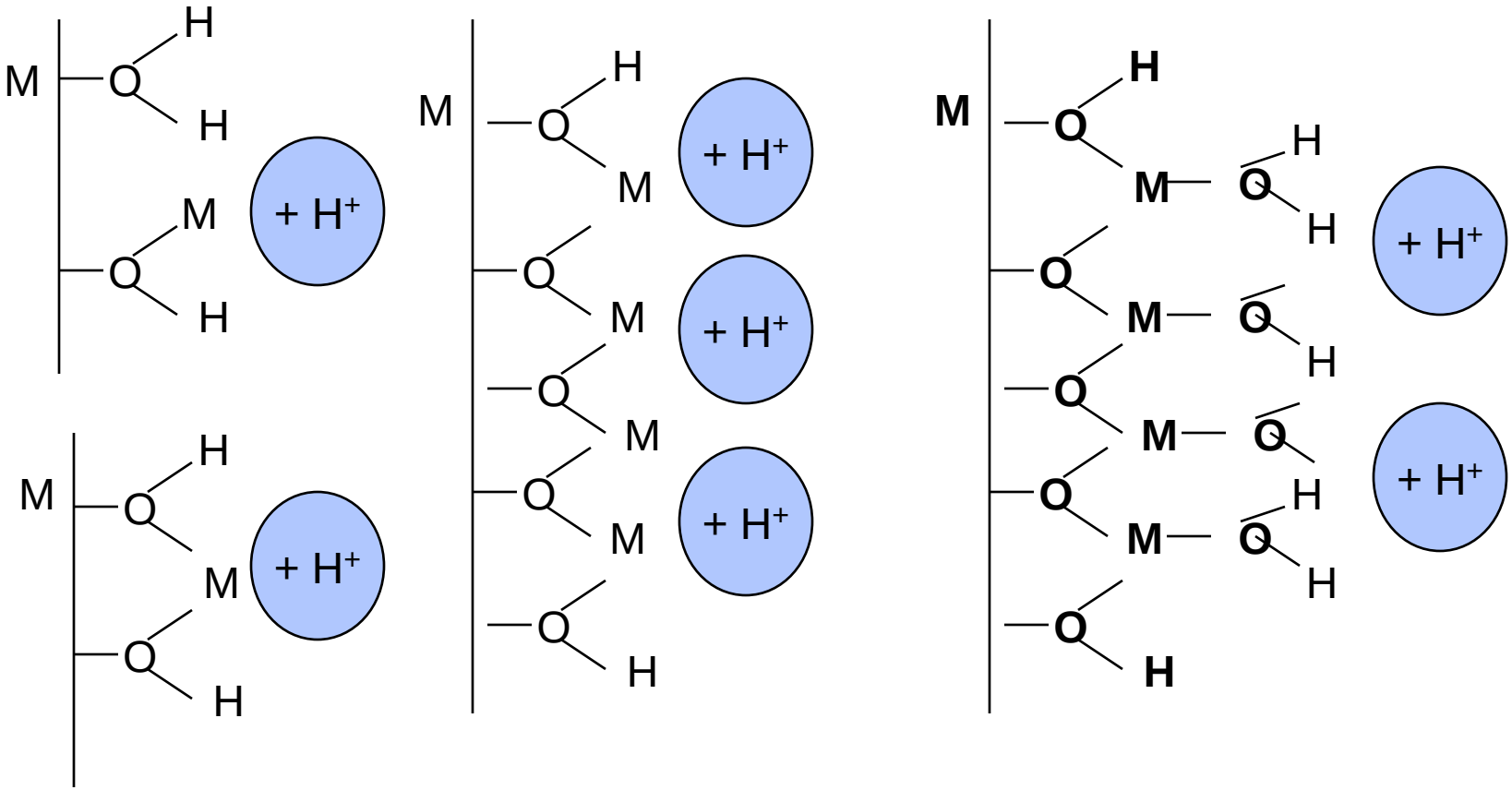
**Bockris mechanism for iron dissolution**

(1) $\mathbf{Fe(OH_2) \rightarrow (FeOH) + H^+ + e^-}$

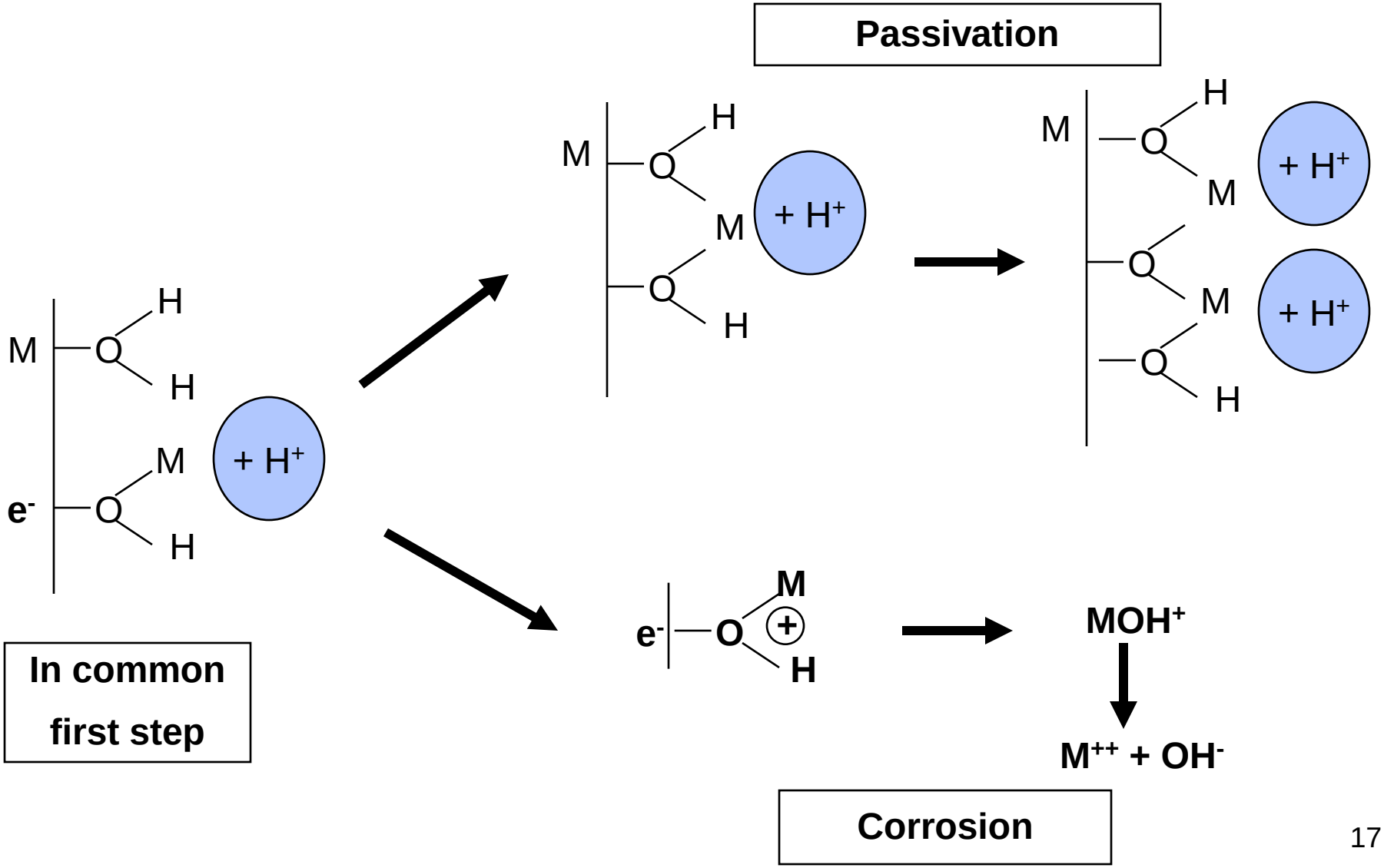
(2) $\mathbf{(FeOH) \rightarrow (FeOH^+) + e^-}$

(3) $\mathbf{(FeOH^+) \rightarrow Fe^{++} + OH^-}$

# Water passivation



# Competition between water corrosion and passivation processes (summary)



## Chloride assisted corrosion process

*Adsorption of a chloride ion*

**Lewis acid base reaction**

$M \text{ — } Cl^-$

↓

**Oxidation**

$e^- \text{ — } MCl$

↓

**Oxidation**

$e^- \text{ — } MCl^+$

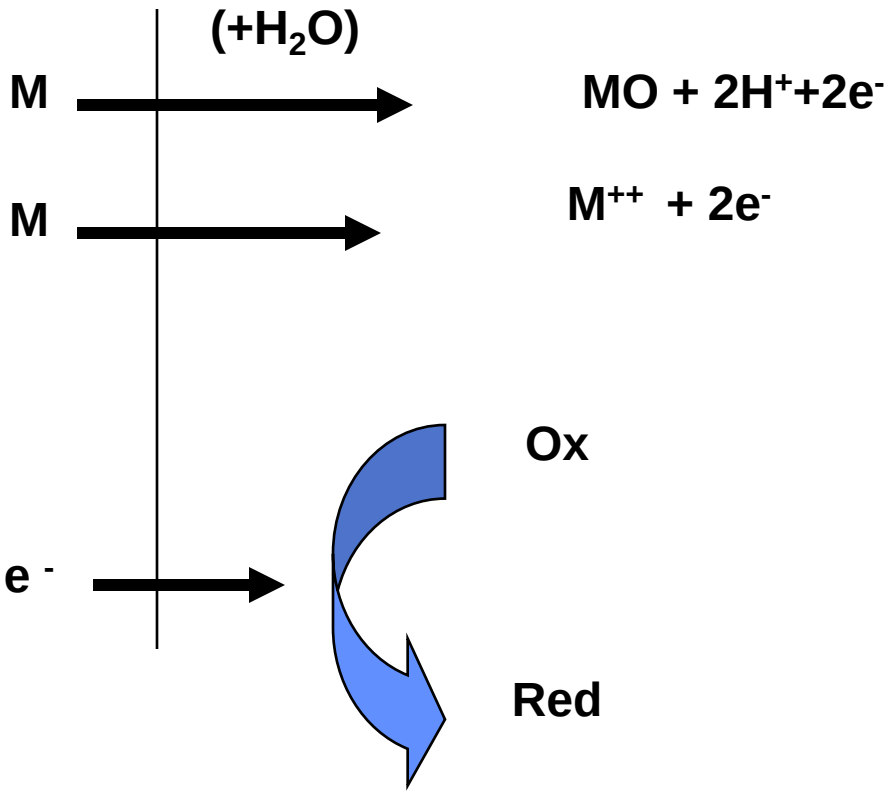
↓

**Dissolution**

$M^{++} + Cl^-$

## Corrosion outlook:

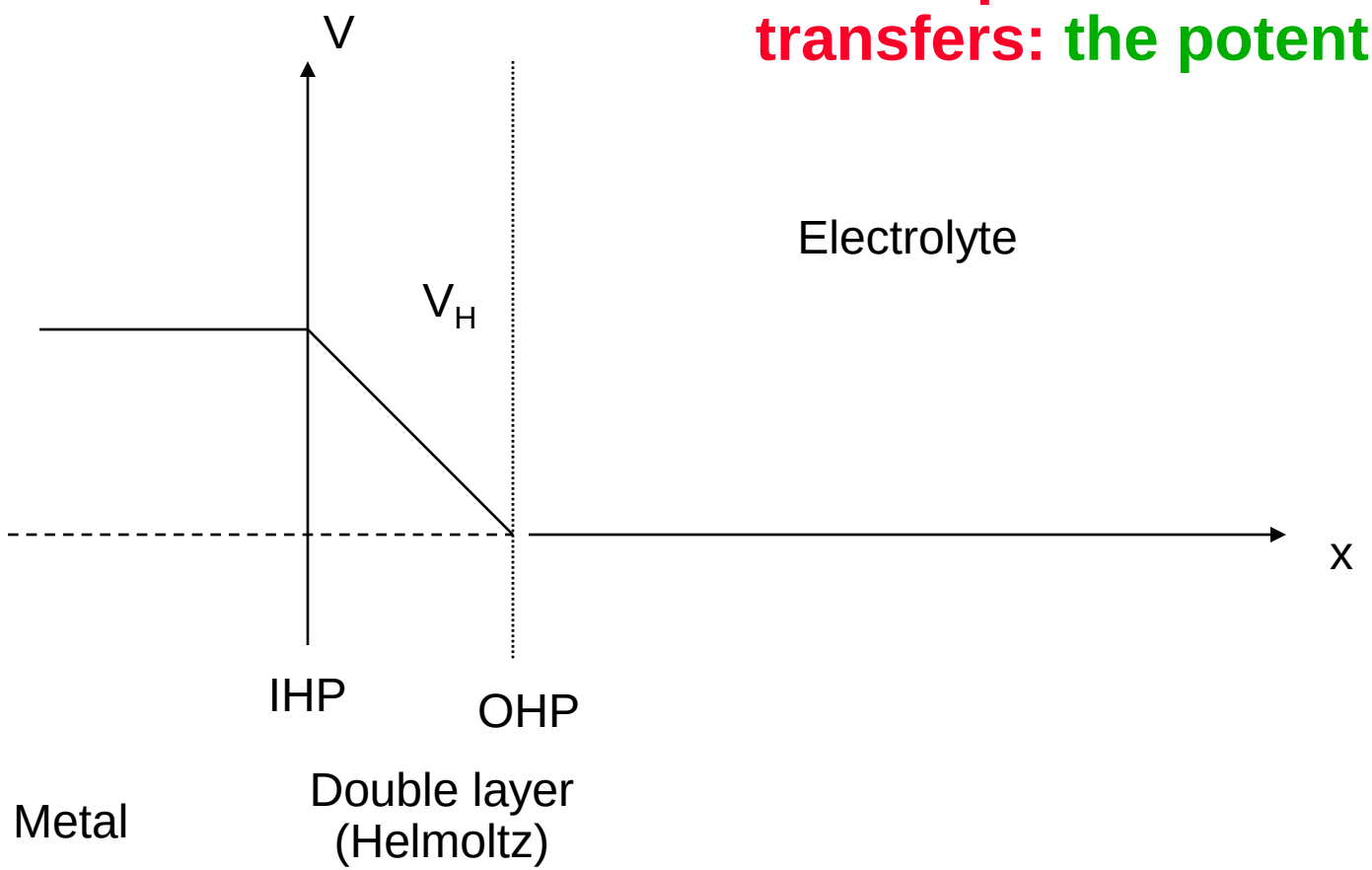
**Anodic**
**(electron producing)**
**and cathodic**
**(electron consuming)**
**reactions**




**Ox +e$^-$ → Red**

$$\begin{cases} 2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2 \\ 2H_2O + O_2 + 4e^- \rightarrow 4OH^- \\ Fe^{+++} + e^- \rightarrow Fe^{++} \end{cases}$$

# Consequence of the charge transfers: the potential drop

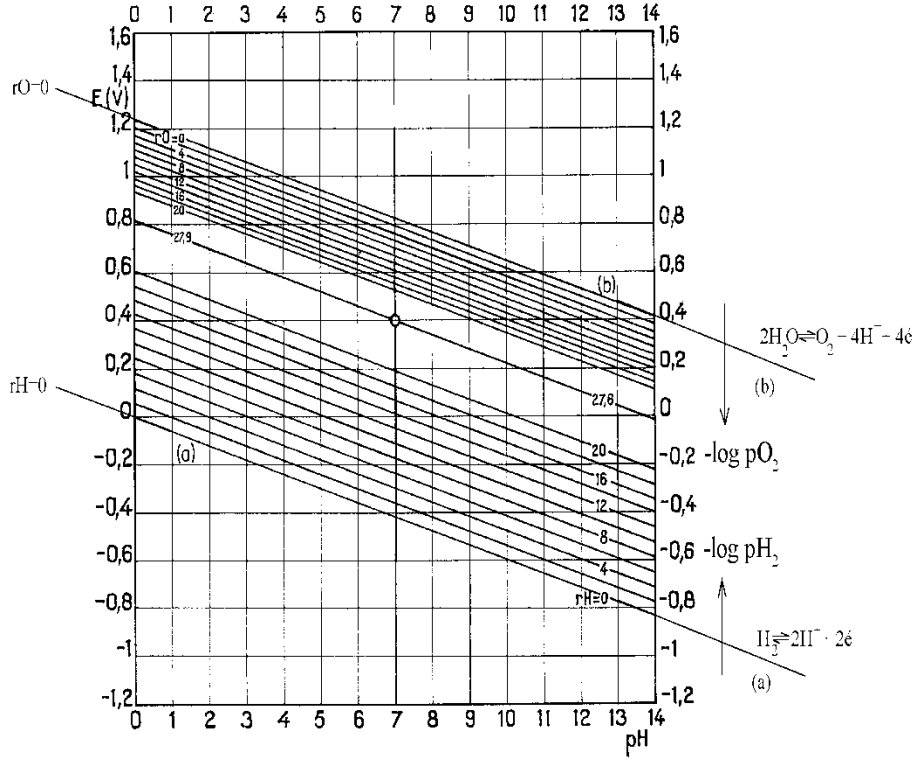



**The Charge transfers (electrons and ions) between the metal and the aqueous solution produces a potential difference**

# Effect of the potential drop on the electrochemical equilibria of water

V is the potential difference between water and the electron reservoir,

The Standard hydrogen electrode (V=0) is defined by pH=0 and p(H2)=1.Atm




## Electrochemical equilibria

$$H_2O + \frac{1}{2}O_2 + 2e^- \leftrightarrow 2OH^-$$

$$H_2O + \frac{1}{2}H_2 \leftrightarrow H_3O^+ + e^-$$

## Law of mass action

$$V = 1{,}23^{Volts} + \frac{kT}{q}(Ln(H^+) + \frac{1}{4}\ln(pO_2)$$

$$= 1{,}23^{Volts} - 60^{mV}(pH - \frac{1}{4}\log(pO_2)$$

$$V = \frac{kT}{q}(Ln(H^+) - \ln\sqrt{pH_2}) = -60^{mV}(pH + \log\sqrt{pH_2})$$

# Corrosion equilibria

**At a metal electrode, several potential and pH dependent reactions occur**

(1) Anodic dissolution:

$$M \leftrightarrow M^{++} + 2e^-$$

(2) Dissolution or Precipitation of the oxide

$$M^{++} + H_2O \leftrightarrow MO + 2H^+$$

(3) Passivation

$$M + H_2O \leftrightarrow MO + 2H^+ + 2e^-$$

**Assuming local equilibria, the mass action law writes**

$$V = cst. + 2.3\frac{kT}{2q}\log(c)$$

$$pH + \frac{1}{2}\log(c) = cst.$$

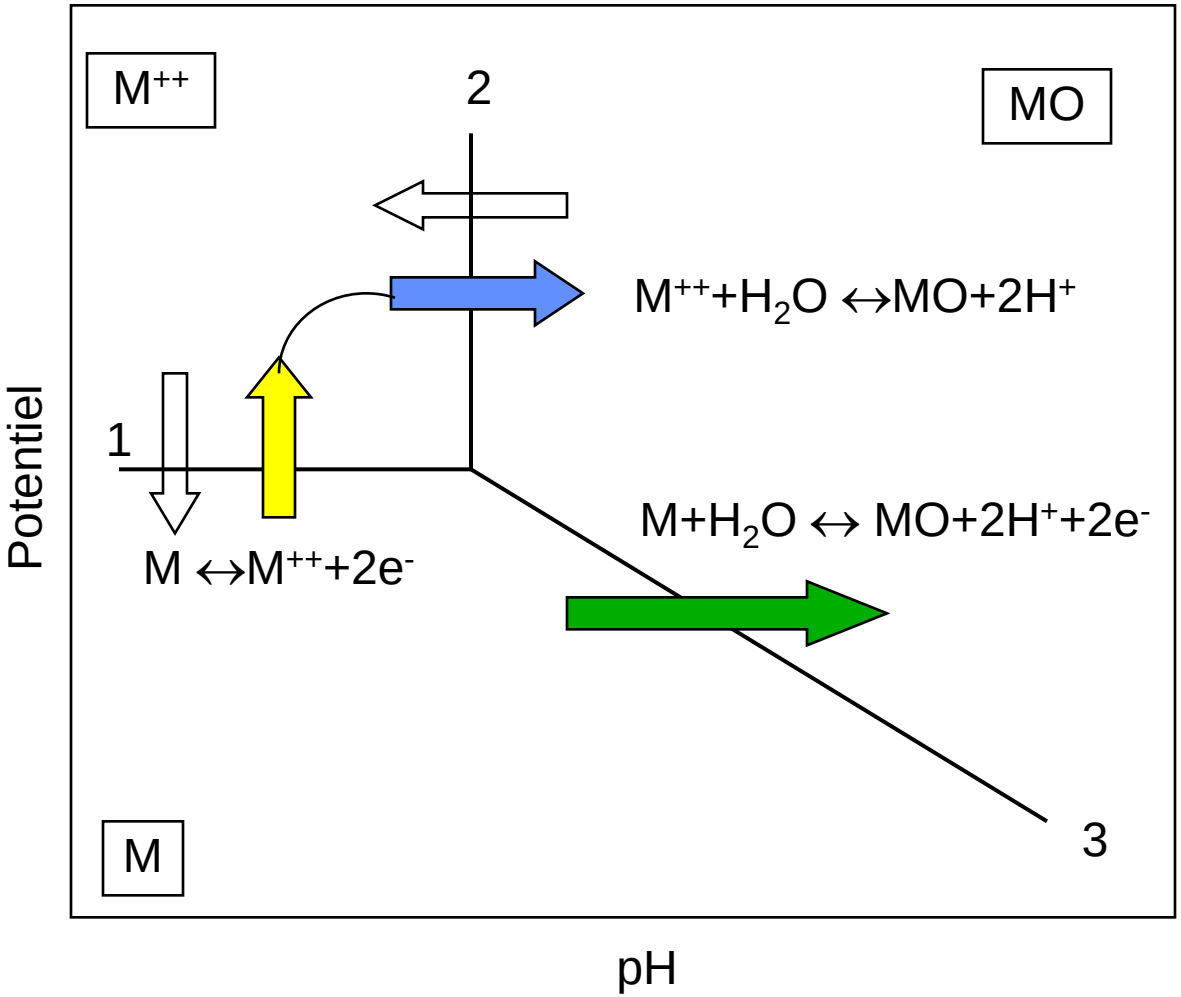
$$V + 2.3\frac{kT}{q}pH = cst.$$

Where ***c*** is the concentration in dissolved cations near the metal interface.

***C*** results from the balance between the dissolution rate and the diffusion flow ***J*** □ ***c*** from the metal surface to the solution bulk (where c=0)

The dissolution rate is then proportionnal to ***c***

# The Pourbaix diagrams of metals




$$c = \left[M^{++}\right]$$

$$(1)\, V = cst. + 2.3\frac{kT}{2q}\log(c)$$

$$(2)\; pH + \frac{1}{2}\log(c) \;= cst.$$

$$(3)\, V + 2.3\frac{kT}{q}\, pH = cst.$$

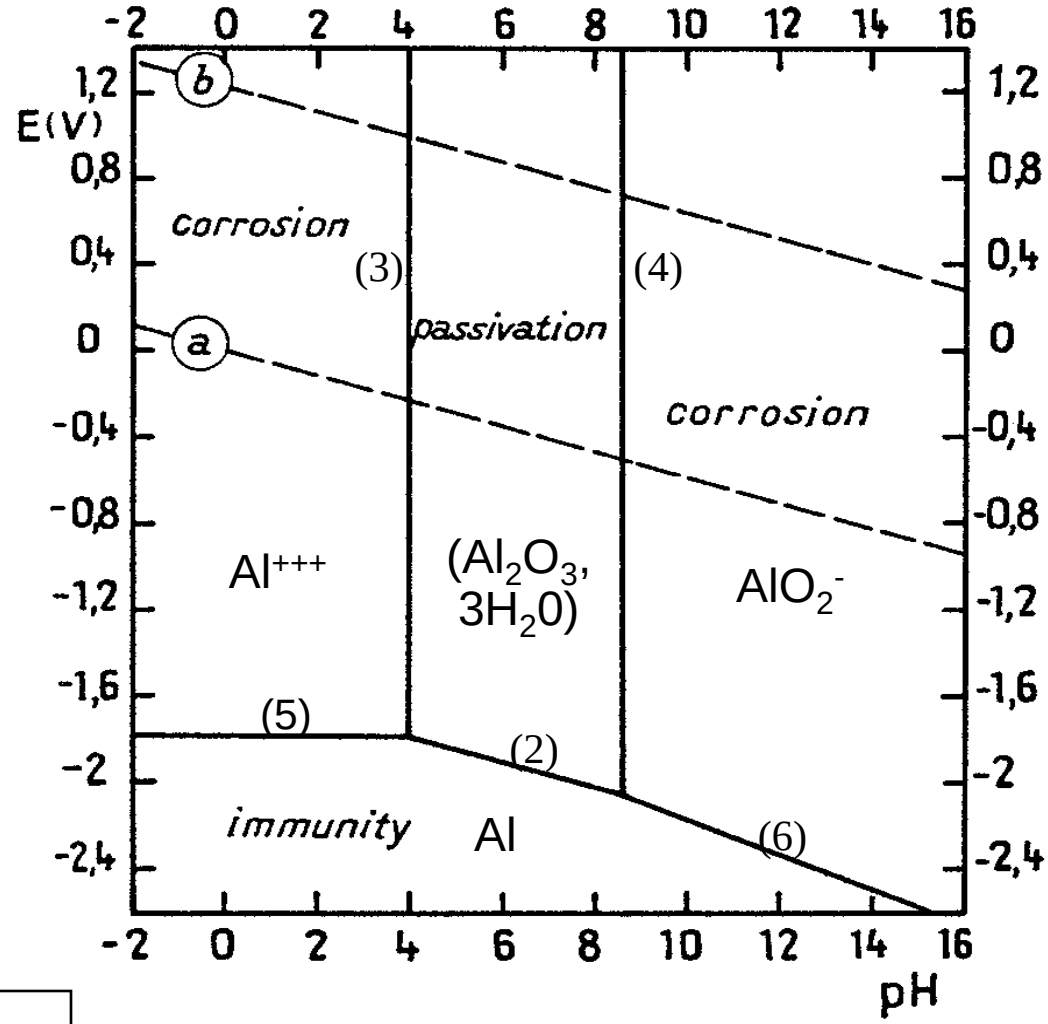
**$M \rightarrow M^{++}$ : anodic dissolution**

**$M \rightarrow MO$ : passivation**

**$M^{++} \rightarrow M0$ : rust precipitation**

***In diffusion controlled kinetics,*** *the corrosion current* **j** *is proportionnal to the concentration* **c** *in solute cations near the surface. An arbitrary concentration* **c =$10^{-6}$M** *is chosen, below wich corrosion is disregarded*

# Pourbaix diagram of Aluminium




(1) $Al^{+++} + 2\ H_2O \leftrightarrow AlO_2^- + 4\ H^+$

(2) $Al + 3\ H_2O \leftrightarrow Al_2O_3 + 6\ H^+ + 6\ e^-$

(3) $2\ Al^{+++} + 3\ H_2O \leftrightarrow Al_2O_3 + 6\ H^+$

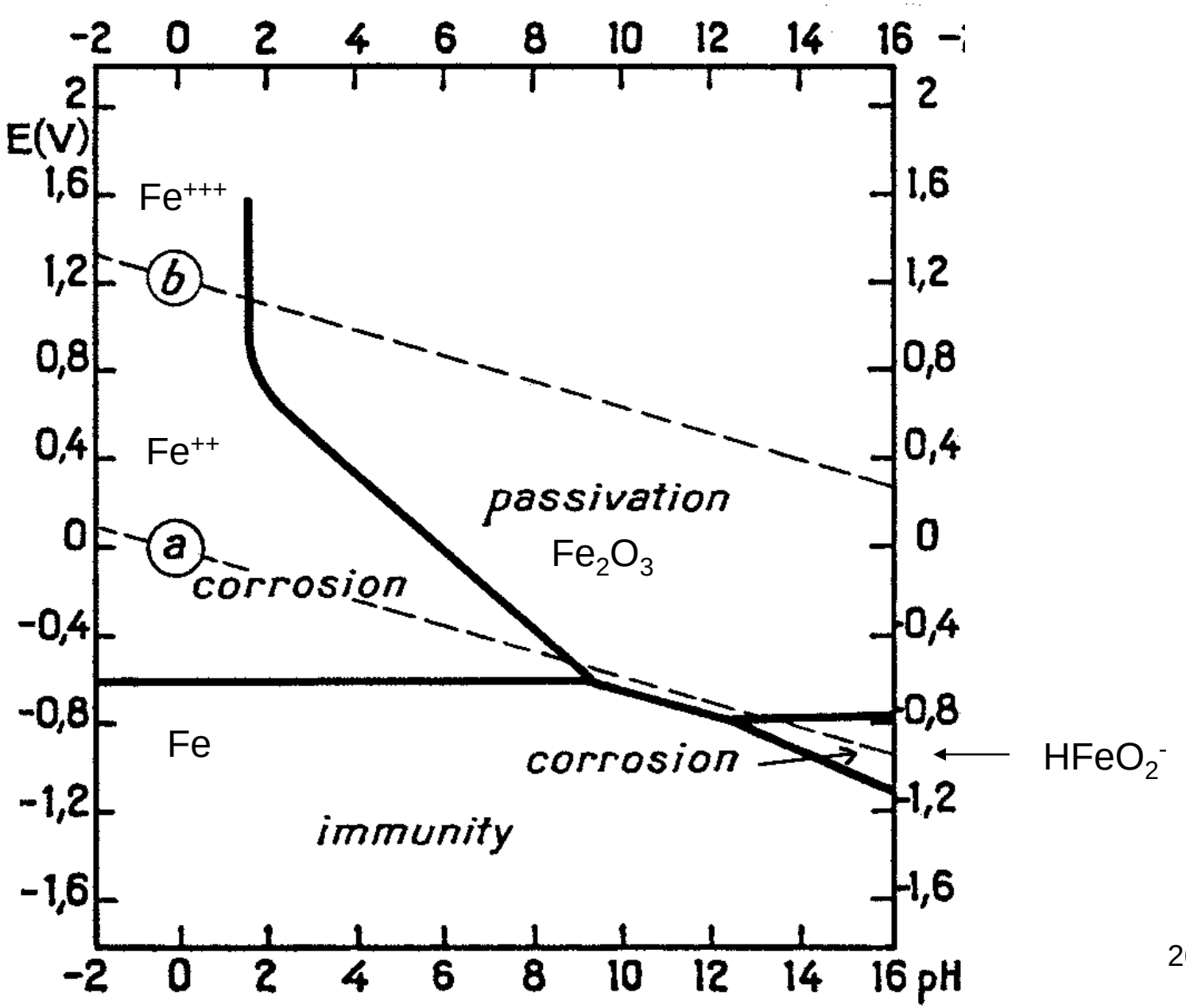
(4) $Al_2O_3 + H_2O \leftrightarrow 2\ AlO_2^- + 2\ H^+$

(5) $Al \leftrightarrow Al^{+++} + 3\ e^-$

(6) $Al + 2\ H_2O \leftrightarrow AlO_2^- + 4\ H^+ + 3\ e^-$

NB: this diagram is drawn for 1µM/l concentrations in solute species

# Pourbaix diagram of Iron



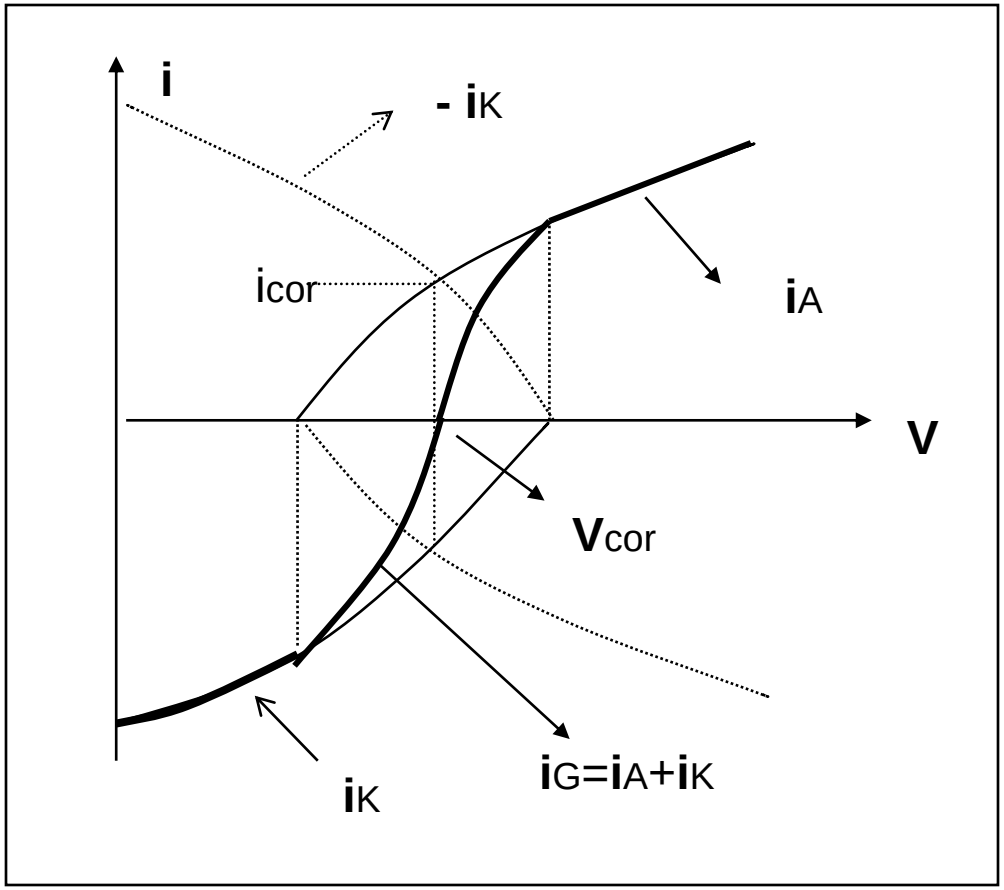
# Effect of the potential drop on the Corrosion kinetics.
## Polarisation curves:

**Both anodic and cathodic currents depend on the potential difference**

**V = Electrode potential**

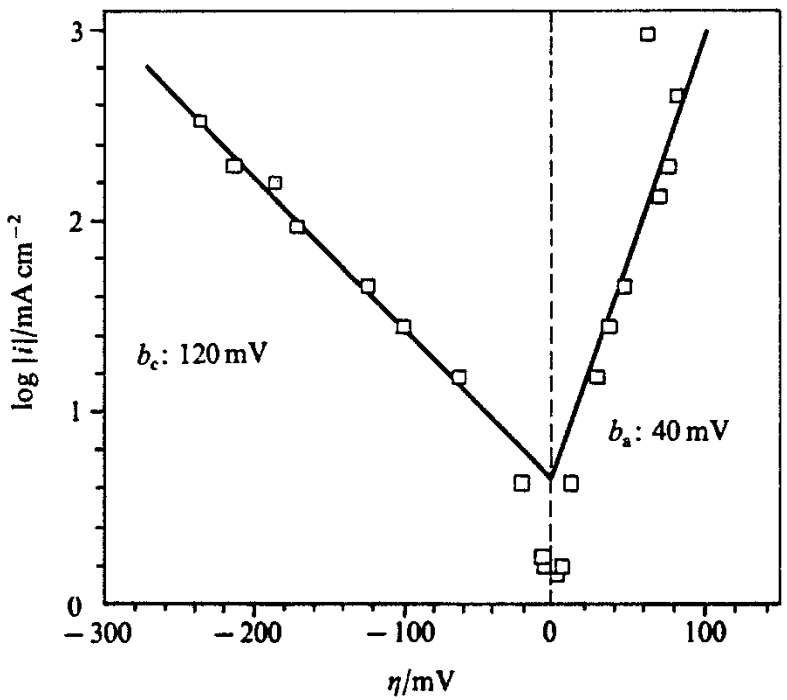
**$V_{cor}$ = Corrosion potential**

**I = Current density**



# The Tafel law

CU in $H_2SO_4$(0.5M) + $CuSO_4$(0.075M)



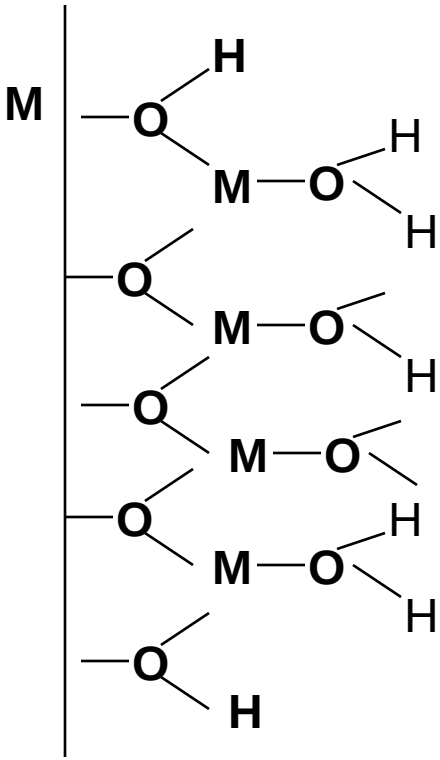

**The Tafel law:** $\boxed{V = cst + b \log i}$ **I = B.exp (2.3 V/ b)**

In the cathodic domain: Proton reduction

In the anodic domain: Anodic dissolution

# Part II) Passive films

**From passive layer to passive film:**
**ion hopping and water deprotonation**

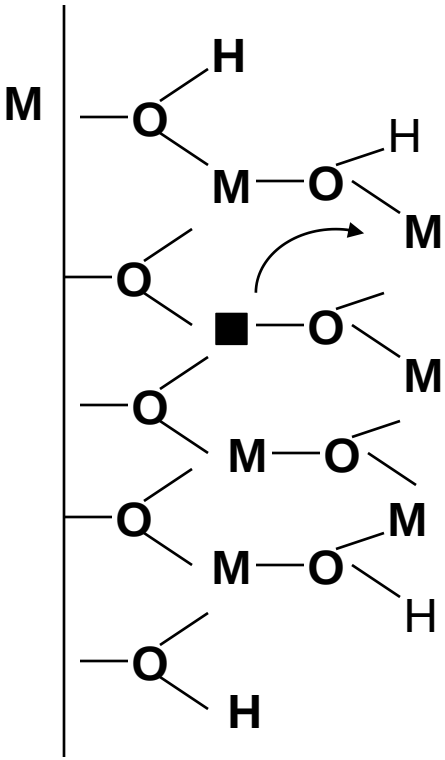



**(a) Formation of the first oxide monolayer**

**(b) Cation hopping and formation of a second layer.**

**(c) Vacancy ■ migrates toward the metal**

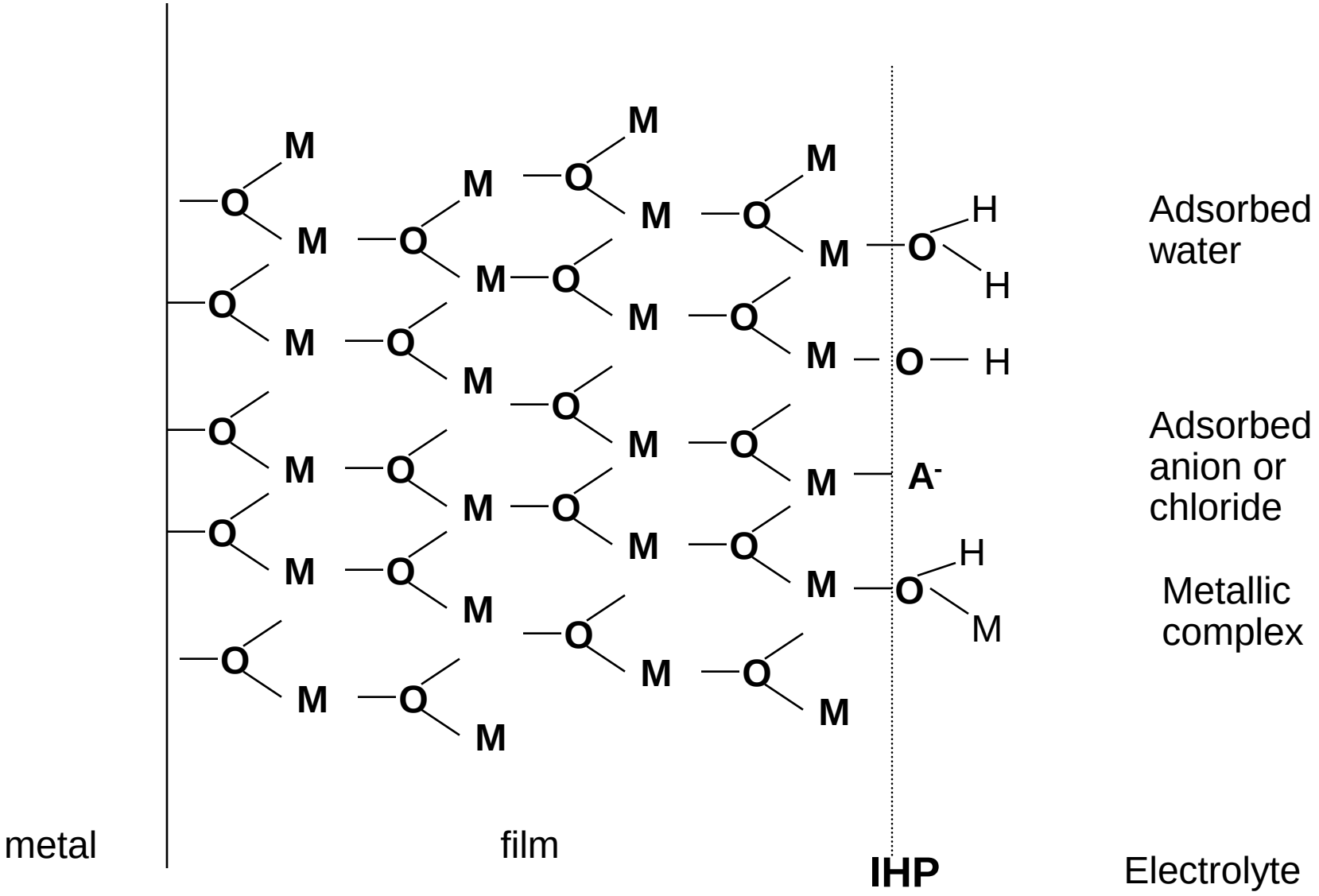
**(d) The process is repeated (Passive Film growth)**




**(a) First (hydrated) oxide layer**

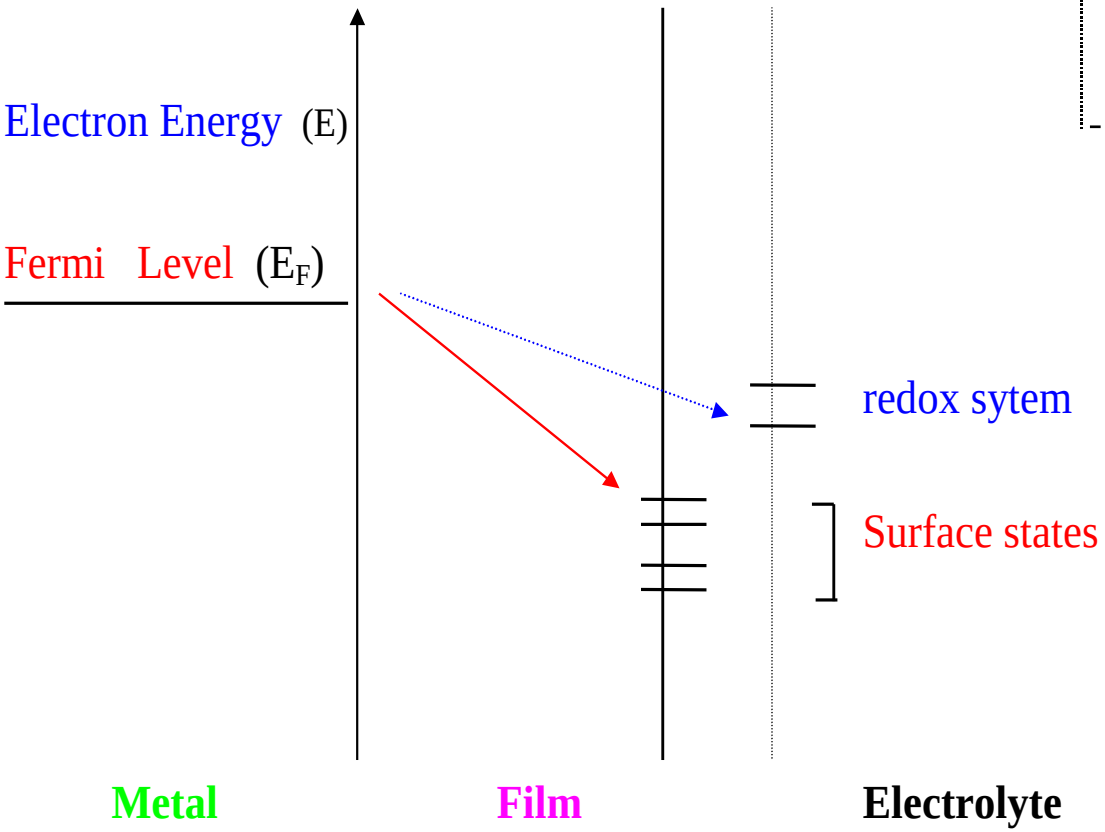
**(b) ion hopping and film growth**

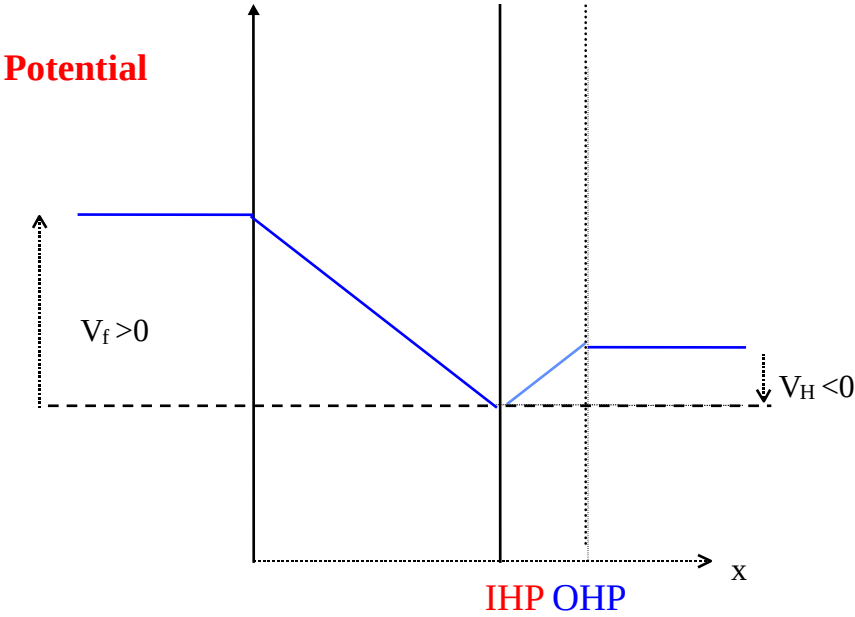
# (over)simpified model of passive film




*Thickness: few nanometers*

# The Electric field




L ~ 30 A° (example)

**F~$10^6$ V/cm= 10mV/Å**

**Electron transfer from metal to electrolyte redox system (e.g. $Fe^{+++}/Fe^{++}$) or on metallic complexes ($MOH^+$ type) located at IHP**

Density: $F = \sigma_{ss}/\varepsilon \sim 10^6$ V/cm $\Leftrightarrow \sigma_{ss}/q \sim 10^{14}$ $cm^{-2}$

# Effect of the electric field

- **Ionic conduction**
  - The electric field drives the positively charged species (cations, anionic vacancies…) toward the outer interface, and the negatively charged species (anions, cationic vacancies …) toward the inner interface

- **Electrostriction**
  - Strong electric field produce a so called electrostriction force, perpendicularly to the field, This force is normally equilibrated by the cohesion forces in the oxide. A decrease in these cohesion forces may therefore produce local breakdown of the passive film (Sato)

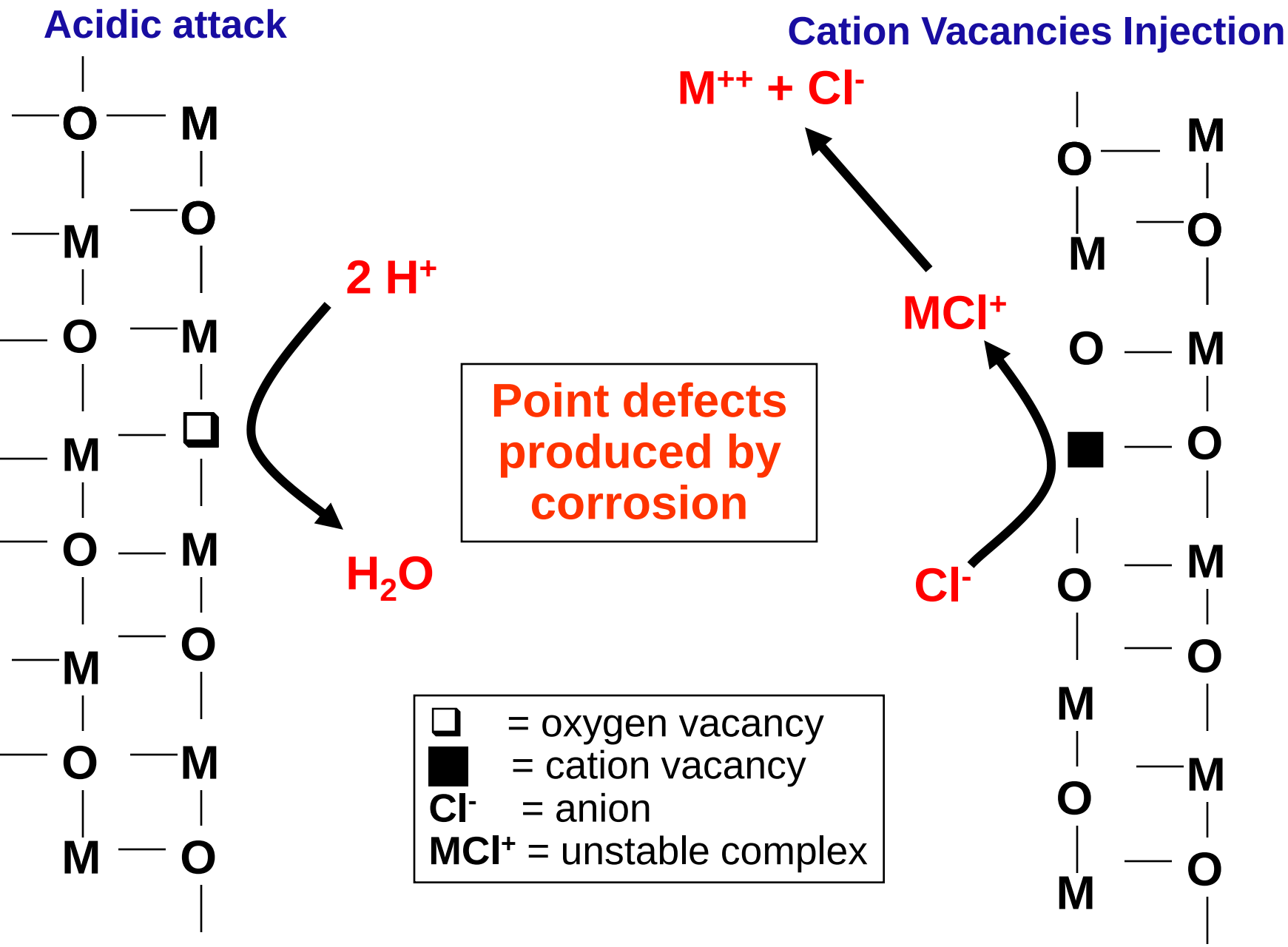
# Défauts ponctuels

**Pour les films passifs minces, on considère généralement que la densité en défauts ponctuels (ions en excès et lacunes) est très faible:**

$$\rho << 1/L^3 \sim 10^{20}\ cm^{-3} \quad \text{(pour L ~ 2nm)}$$

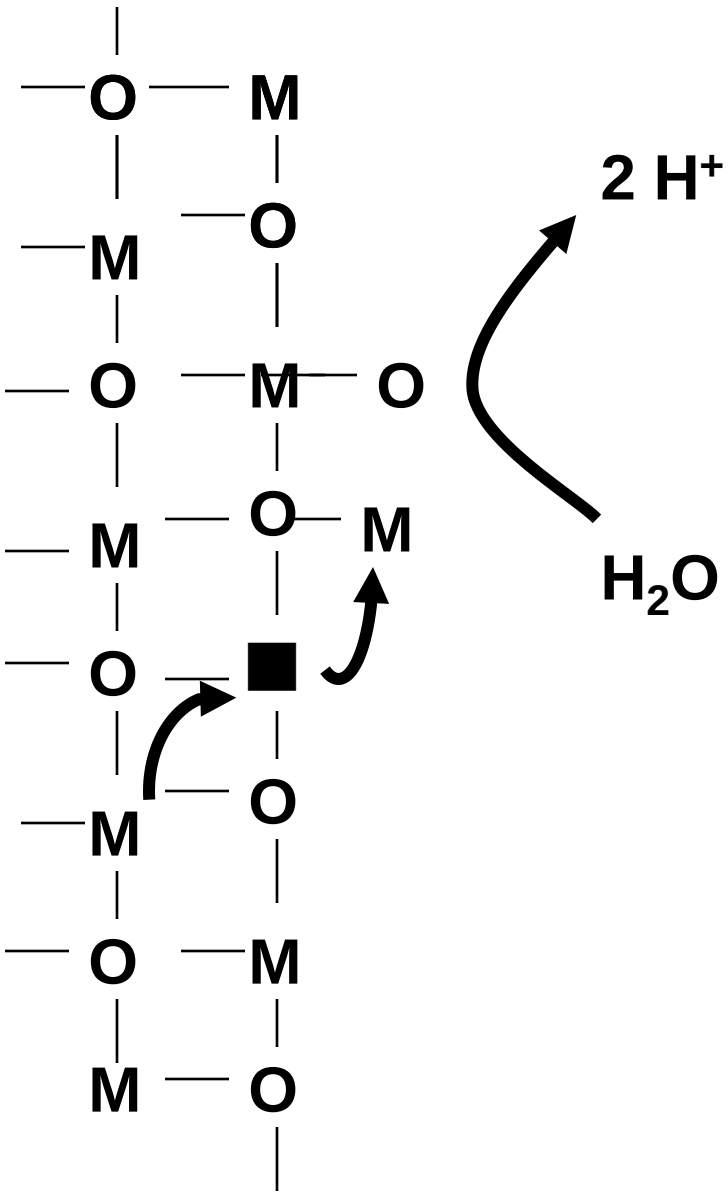
**Les défauts ponctuels sont chargés et agissent comme pièges électroniques**

**Suivant leur charge, ils migrent vers le métal ou l'interface externe qui peuvent constituer des sources ou des puits de défauts.**




Cation vacancies migrate toward the metal film interface where they anihilate

## Oxygen deposition



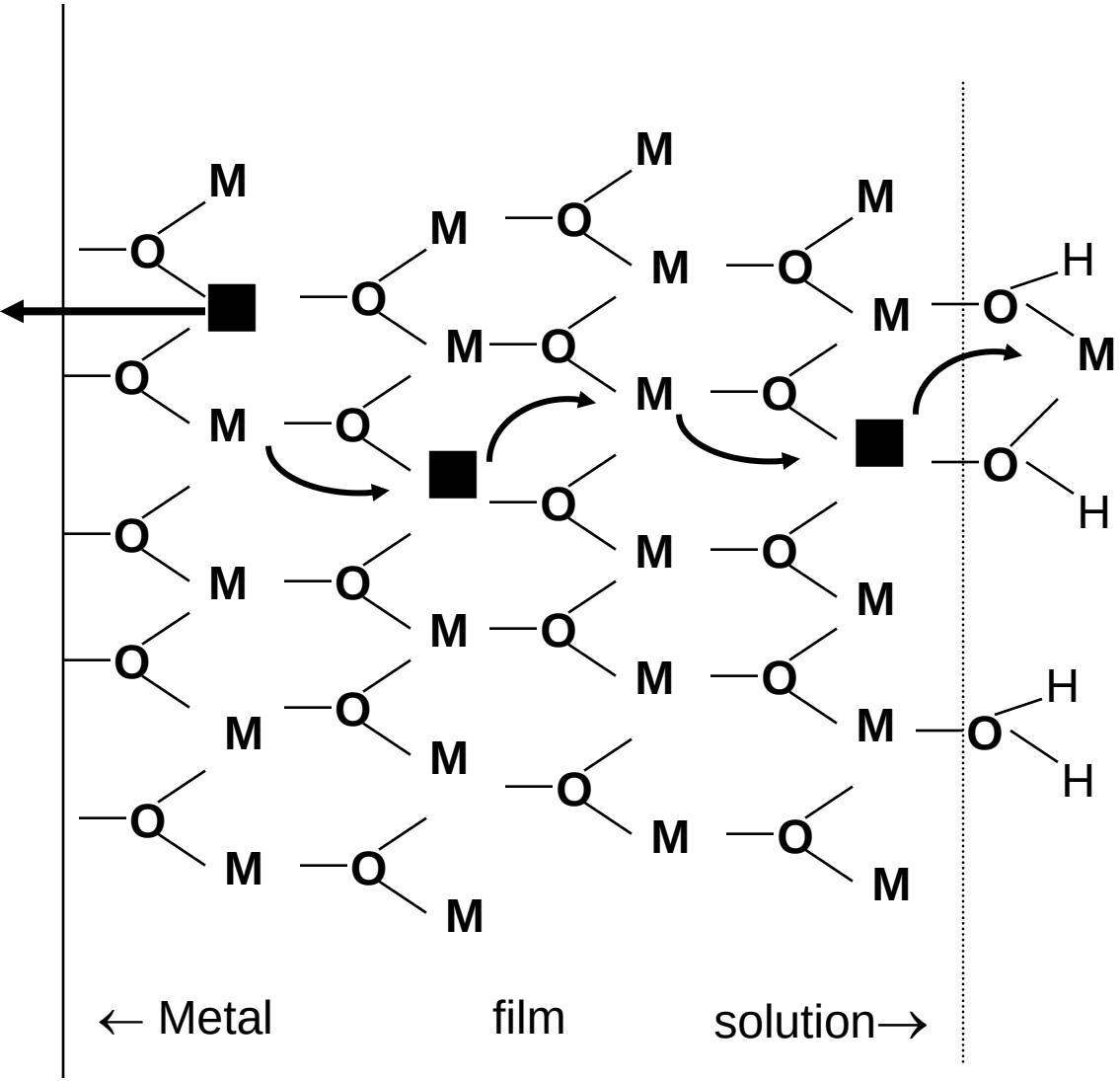

**Water deprotonation produces Oxygen anions excess**

**Cation hopping ⇒ film growth**

Growth kinetics is controlled by the cation migration rate from the mf interface ( ⇔ vacancies migration to the mf interface)

**Cation vacancies produced by the film growth**

# Croissance des films (details)




- **Un cation est transféré du film vers le film hydraté d'extrème surface où il prend la place d'un proton qui est rejeté en solution**
- **Le processus global se résume à une déprotonation de l'eau et à une injection de lacunes cationiques dans le film**
- **Sous l'effet du champ électrique les lacunes cationiques créées sont drainées par le champ électrique vers l'interface métal-film où elles s' anihilent**

# Capacité de croissance

La Croissance du film implique le transfert d ’une charge par unité de surface:

$$dQ = \frac{Zq}{\delta^3} dL$$

où $\delta^3$ est le volume cationique moyen et $\nu = \frac{Zq}{\delta^3}$ ~ 18 Cb/mm$^3$ dans le cas de $ZrO_2$

Et engendre une augmentation dV de chute de potentiel V=F.L à travers le film:

**dV=FdL+**LdF**.**

if dF~0 then **F= dV/dL = ν / C**

**C=ν /F** est la **capacité de croissance**

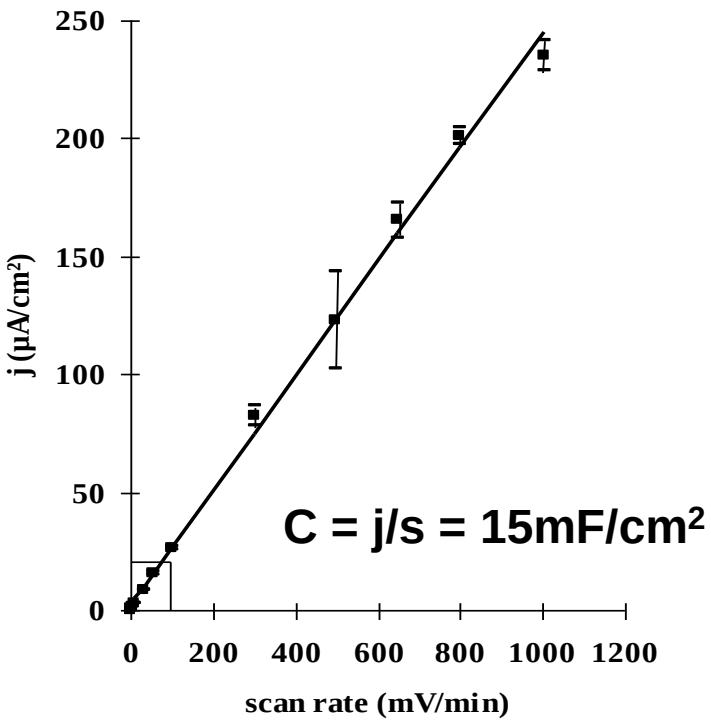
**C = 15 mF/cm²**

pour F = 1.2 10$^6$ V/cm (1/F~8 nm/V)

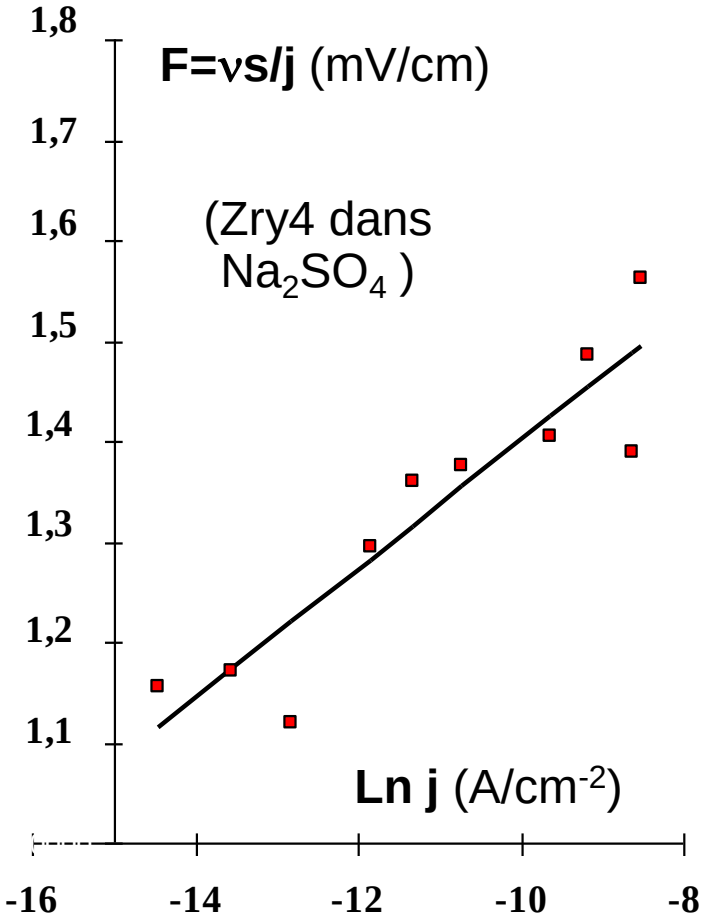
**L’augmentation de potentiel** d ’électrode est entièrement absorbée par **la croissance du film**

**Zry4** poli 4000 dans $Na_2SO_4$ 1M pH 6.6 23°C désaéré. Tracé de courbes de polarisation à plusieurs vitesses de balayage s . Le courant mesuré est sensiblement constant dans le domaine passif. j est sa valeur pour V = 1 V/SCE.

la Capacité **C = j/s = jdt/dV = dQ/dV** est sensiblement constante et proche d ’une capacité de croissance.



# Loi du Champ fort
## (mise en évidence expérimentale)




Une analyse plus fine des résultats précédents montre que **C=j/s** et donc aussi **F = νs/j** ne sont pas rigoureusement constants et varient linéairement avec **Ln j** :

$$F = \nu s/j = F^*.\mathrm{Ln}(j/j^*)$$

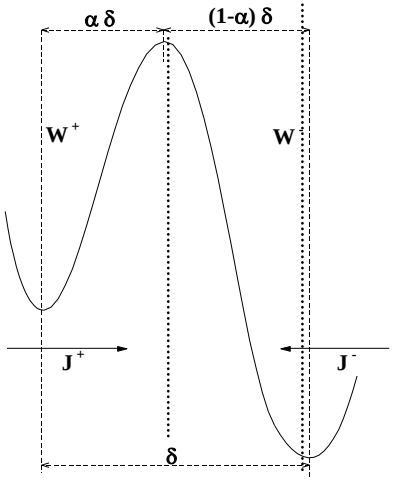
Avec $F^* = 9\ 10^4$ V/cm

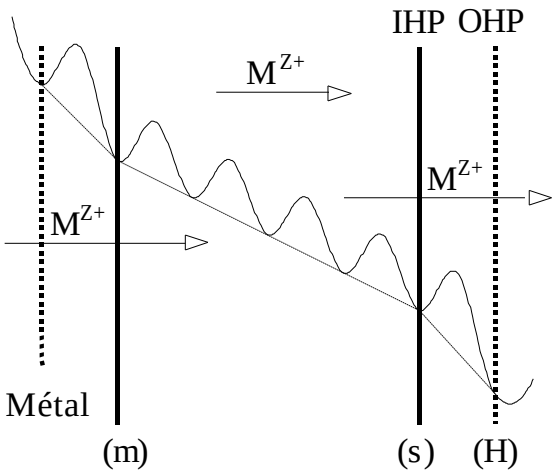
$j^* = 0{,}7.10^{-9}$ A/cm$^2$

D 'où la **loi** dite **du Champ fort** :

$$\boxed{j = j^* \exp \frac{F}{F^*}}$$

# Loi du Champ fort:
## justification théorique




**Transport thermiquement activé:**

$J^+ = K_0 \exp -W^+/kT$

**Effet du Champ électrique:**

$W^+ = W_0 - ZqF\alpha\delta$

$$\Rightarrow J = K(\exp ZqF\alpha\delta/kT - \exp -ZqF(1-\alpha)\delta/kT$$

$\alpha = 0{,}5 \Rightarrow$ $$J = 2KF^* \sinh \frac{F}{F^*}$$

Où 2K est la conductivité et $F^* = \dfrac{kT}{Z\alpha q\delta}$

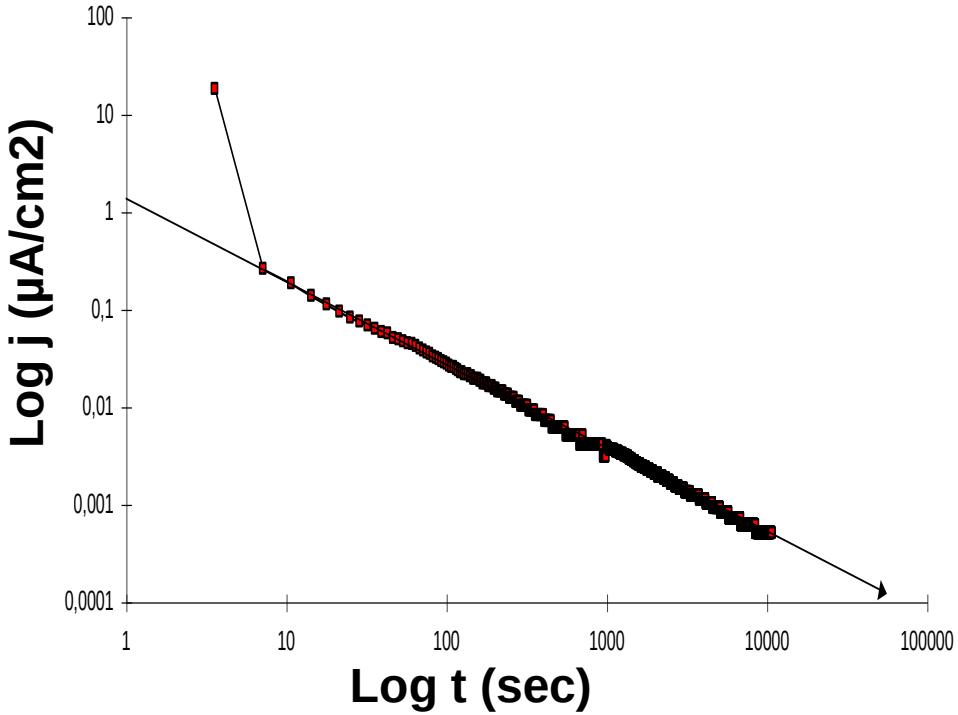
pour $Z\alpha=2$ et $\delta$~1 nm) on trouve:

$$F^* \sim 10^5 V/cm$$

**Loi d 'Ohm**: $F << F^* \Rightarrow J = 2K.F$

**Loi du Champ Fort :** $F >> F^* \Rightarrow J = K.\exp \dfrac{F}{F^*}$

# Loi de croissance en mode potentiostatique
## (Loi Logarithmique Directe)




**Chronoampèremétrie potentiostatique**

Réalisée sur Zry4 poli 4000 polarisé à 1 V/SCE dans Na2SO4 1M pH 6.6 23°C désaéré.

**m = d (Ln j )/d (Ln t) → -1 quand t → ∞**

**Approximation au premier ordre**

**$LF=L_0F_0=V_f=cst.$** $\Rightarrow LdF+FdL=0$

$\Rightarrow F_0(L-L_0)+ L_0(F-F_0) =0$

$\Rightarrow F/F_0=2 -L/L_0$

$dL/dt =cst. \text{ Exp } F/F^* \Rightarrow$

$$\boxed{L-L_0 = a.\ Ln(1+t/\tau)}$$

(Où a et $\tau$ sont des constantes vis-à-vis du temps, mais dépendent de $V_f$ )

$j = \nu.dL/dt = \nu a/(1+t/\tau) \quad \Rightarrow$

**Loi de Mott:** $$\boxed{\frac{1}{j} \approx \frac{1}{j_0}(1+\frac{t}{\tau})}$$

# Compléments

## Loi logarithmique inverse

**(Approximation au second ordre )**

L 'approximation au premier ordre pour le champ donne

$F_0$-F = b. Ln(1+t/τ)

En reportant cette valeur dans l 'équation

1/L= F/ $V_f$

on obtient une approximation au second ordre pour L:

$$\boxed{1/L = 1/L_0 - b.\ Ln(1+t/\tau)}$$

## Epaisseur limite

En mode potentiostatique stationnaire

$$\boxed{J = K_{fs} \exp \frac{F}{F*} = \frac{1}{\delta^3} . \frac{dL}{dt} + J_{dis}(V_H)}$$

$\Rightarrow$ L = ↑ (t)

**Une épaisseur limite** $\bar{L} = \frac{V_f}{\bar{F}}$

est atteinte lorsque $F = \bar{F} = F * Ln \frac{J_{dis}}{K_{fs}}$

$$\boxed{\frac{d\bar{L}}{dV_f} = \frac{1}{\bar{F}}}$$ ~$10^{-6}$cm/V=1Å/10mV

**Loi de croissance**

loin de l 'épaisseur limite:

$$\boxed{\frac{dL}{dt} \approx \delta^3 . K_{fs} \exp \frac{F}{F*} = \delta^3 . K_{fs} \exp \frac{V_f}{LF*}}$$

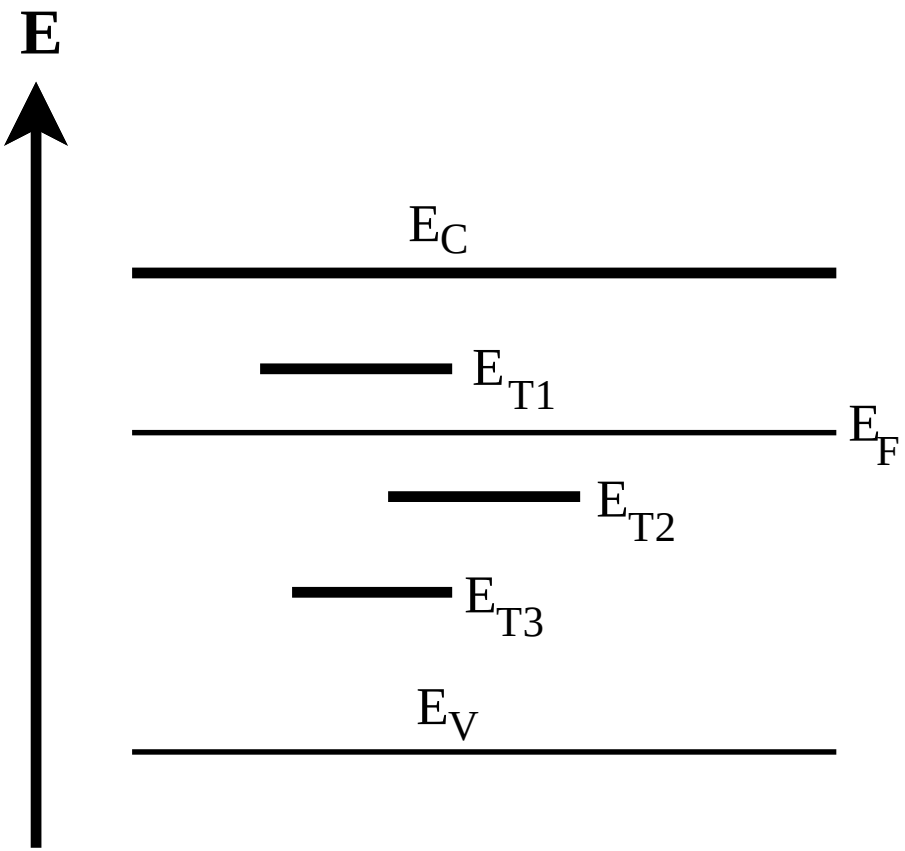
# Les électrons dans le film

L'hypothèse $\sigma_f$**=0** (film non chargé) est totalement arbitraire

**Le film passif est suceptible de contenir des charges ioniques et des charges electroniques (**$\Rightarrow \sigma_f \neq 0$ )

Les Charges ioniques sont constituées par les défauts fonctuels (ions et lacunes) dues à la croissance, a la corrosion , aux défauts de structure, etc…

**Les charges électroniques résultent du piègeage des électrons sur des niveaux accepteurs,** ou à leur dépiegeage à aprtir de niveaux donneurs, en équilibre avec le niveau de Fermi du métal et les niveaux de valence et de conduction de l'oxyde **(comportement semi-conducteur)**




- **Niveau de conduction ($E_c$)**
- **Niveau de valence ($E_v$)**
- **Niveaux pièges ($E_T$)**
- **Niveau de Fermi ($E_F$)**

# Loi d'action de masse et loi de Fermi Dirac

*à l'approximation semi classique*

Soit N(E) le nombre d ' « états » électroniques à l 'énergie E

Chaque « état » électronique peut être vide (oxydé) ou occupé (réduit)

. **Red ↔ Ox + e$^-$** *(metal)*

Un niveau peut être accepteur (neutre si vide, négatif si occupé) ou donneur (neutre si occupé, positif si vide)

On notera ***n*** le nombre d'états occupés et ***N-n*** = nombre d'états vides. La loi d'action de masse s'écrit:

$$n.\exp -E/kT = cst.(N-n).\exp -E_F/kT$$

**La probabilité d 'occupation *n/N*** d 'un état est donc donnée par:

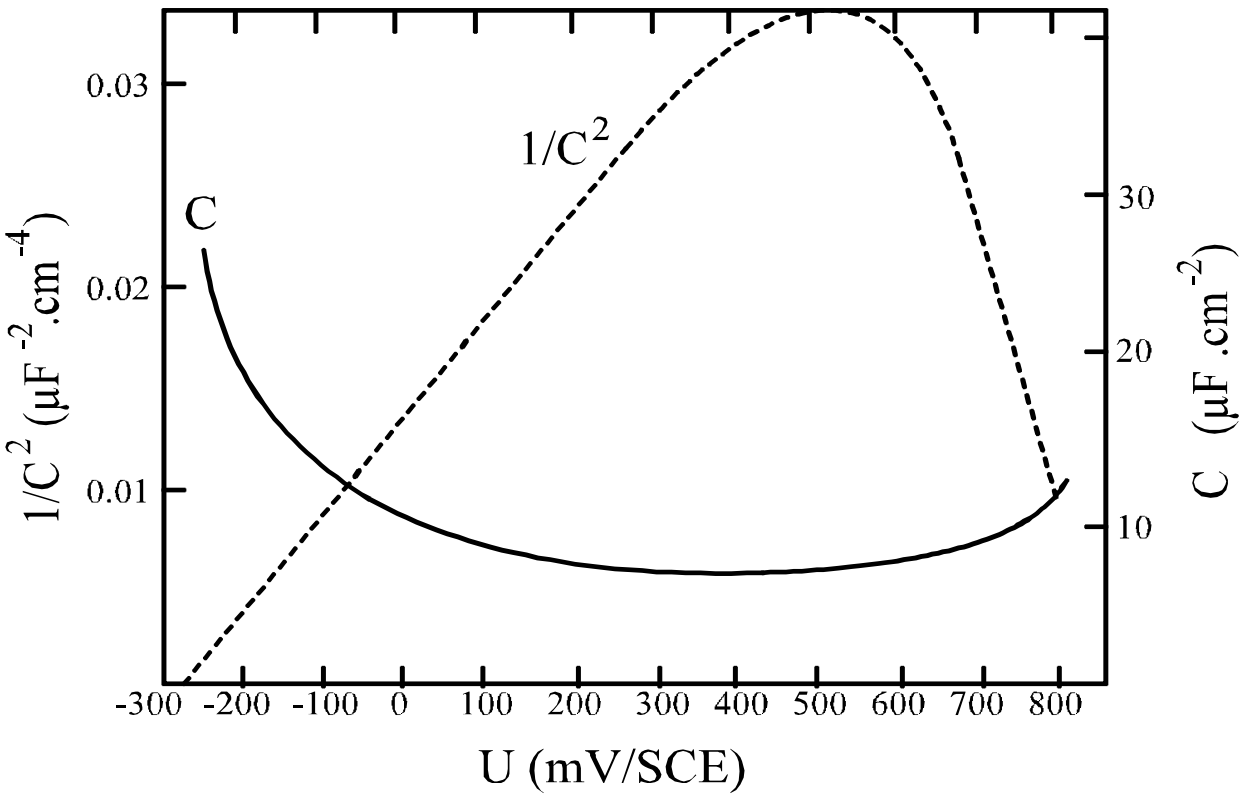
$$\frac{n}{N-n} = \exp\frac{E_F - E}{kT}$$

Qui est formellement analogue à la loi de Fermi-Dirac:

$$\boxed{n/N = \frac{1}{1+\exp\frac{E-E_F}{kT}}}$$

A très basse température, on peut considérer les niveaux d 'énergie comme pleins en dessous du niveau de Fermi, vides au dessus

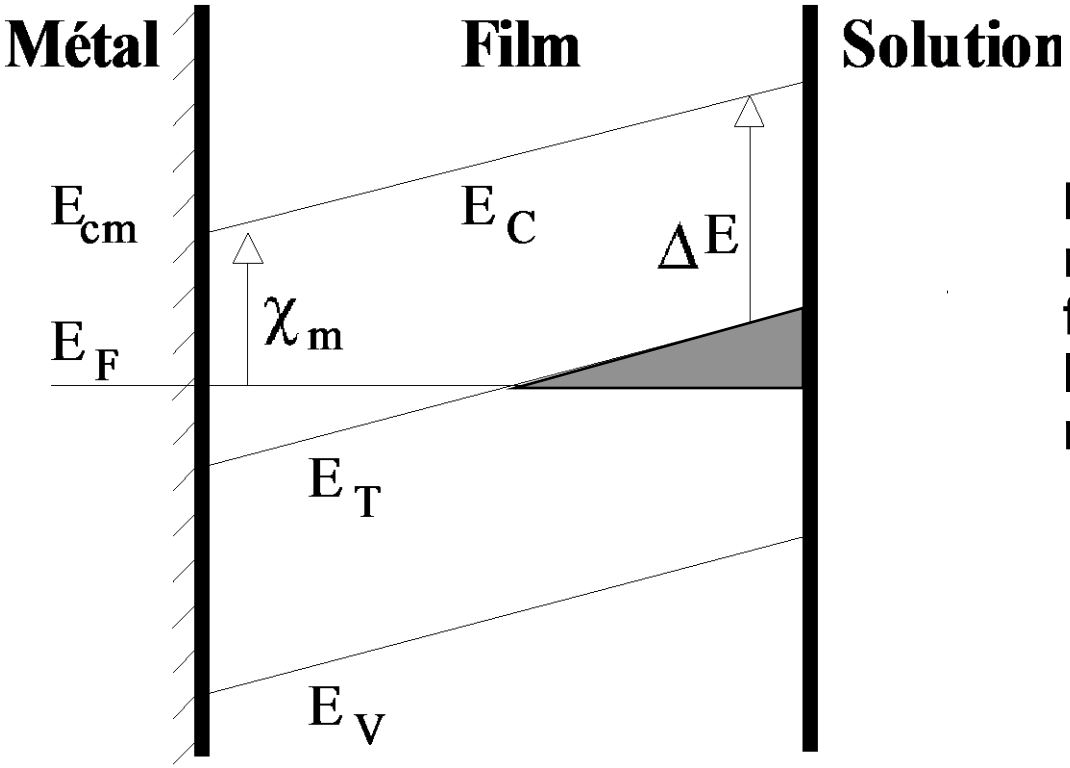
# Mise en évidence des propriétés semi-conductrices des films passifs: comportement de Mott Schottky




Typical $C^{-2}$ vs. V Diagram on an Fe electrode passivated in borate buffer (pH 8,4)

**La Capacité d 'interface suit une loi de Mott –Schottky due au piegeage-dépiegage des electrons dans le film**

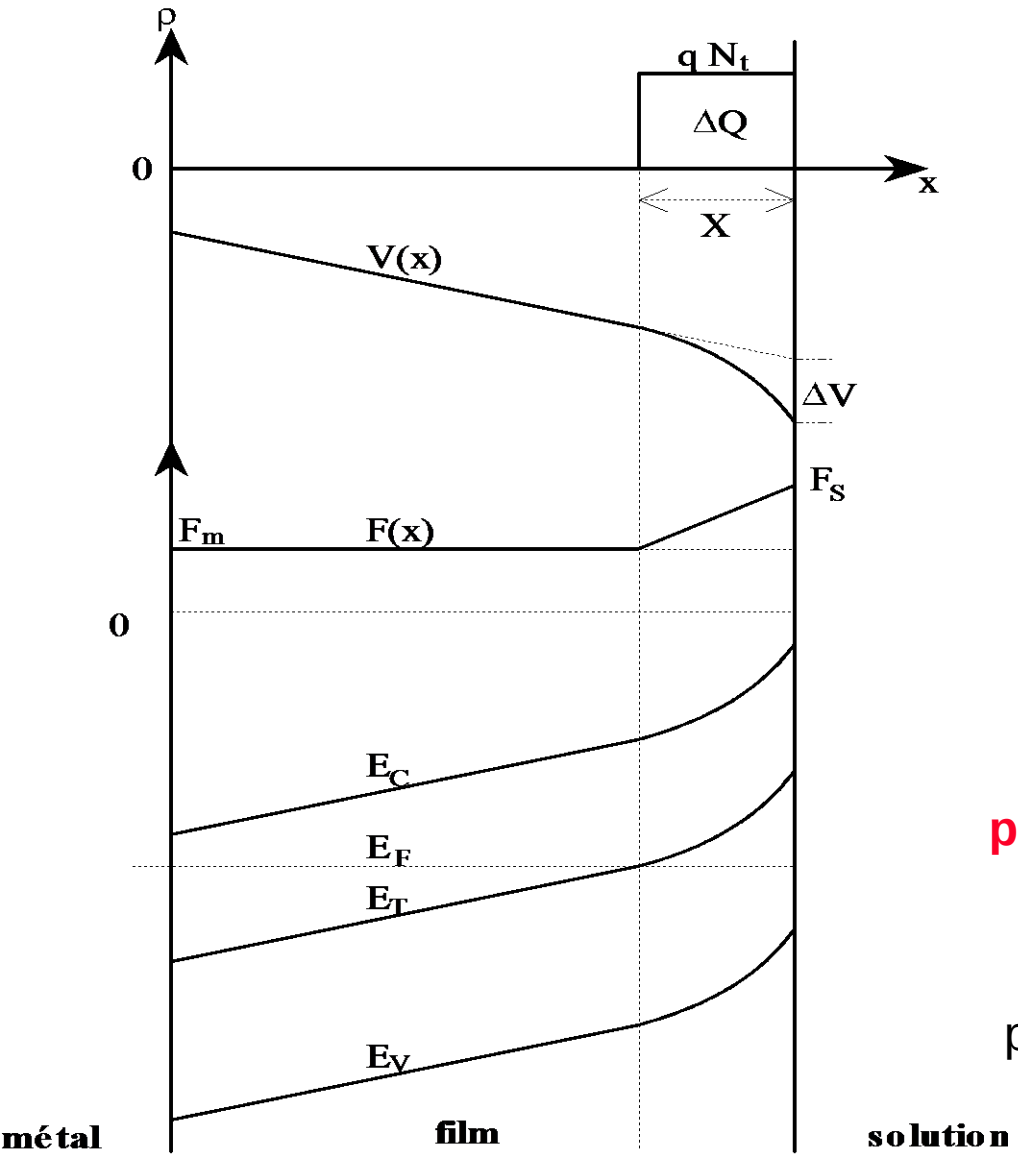
# Effet du champ électrique sur le comportement semi-conducteur des films passifs




**La répartition des niveaux d 'énergie est fortement perturbée par le champ électrique qui règne dans le film**

**Modèle simplifié** : Les niveaux sont remplis en dessous du niveau de Fermi, vides au dessus

# Capacité de Charge d'espace.




$$X = \lambda_D \sqrt{\frac{q\Delta V}{kT}}$$

$$\Rightarrow \quad [\Delta Q]^2 = 2\varepsilon q N \Delta V$$

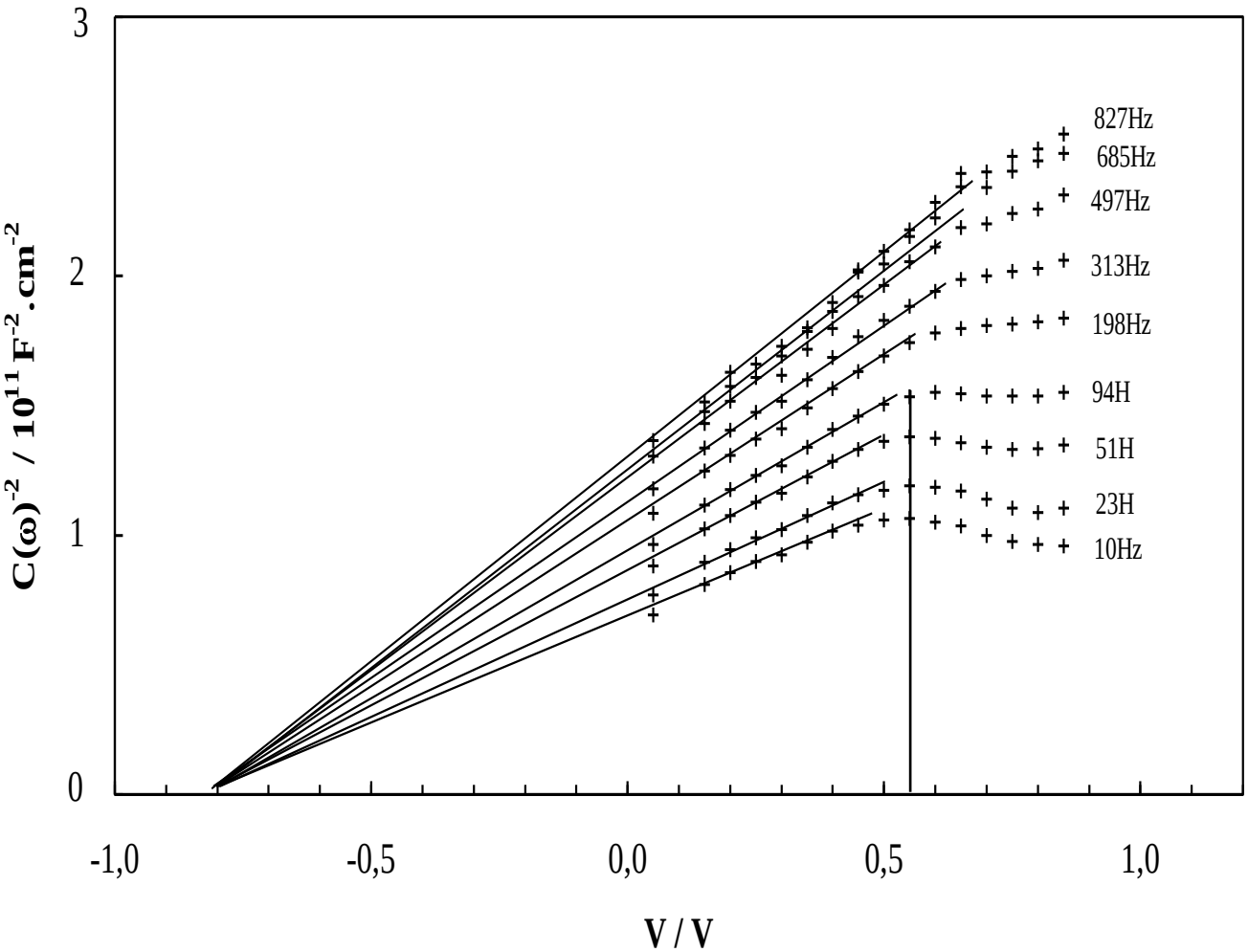
Capacité **C = dΔQ/dΔV**

$$\boxed{\frac{1}{C^2} = \frac{2(V_0 - V)}{N\varepsilon kT}}$$

Où $V_0$ est le
**potentiel de bandes plates** « apparent »

C= 1 µF/cm$^2$

pour N= $10^{20}$ cm$^{-3}$ et V-$V_0$ = 200 mV



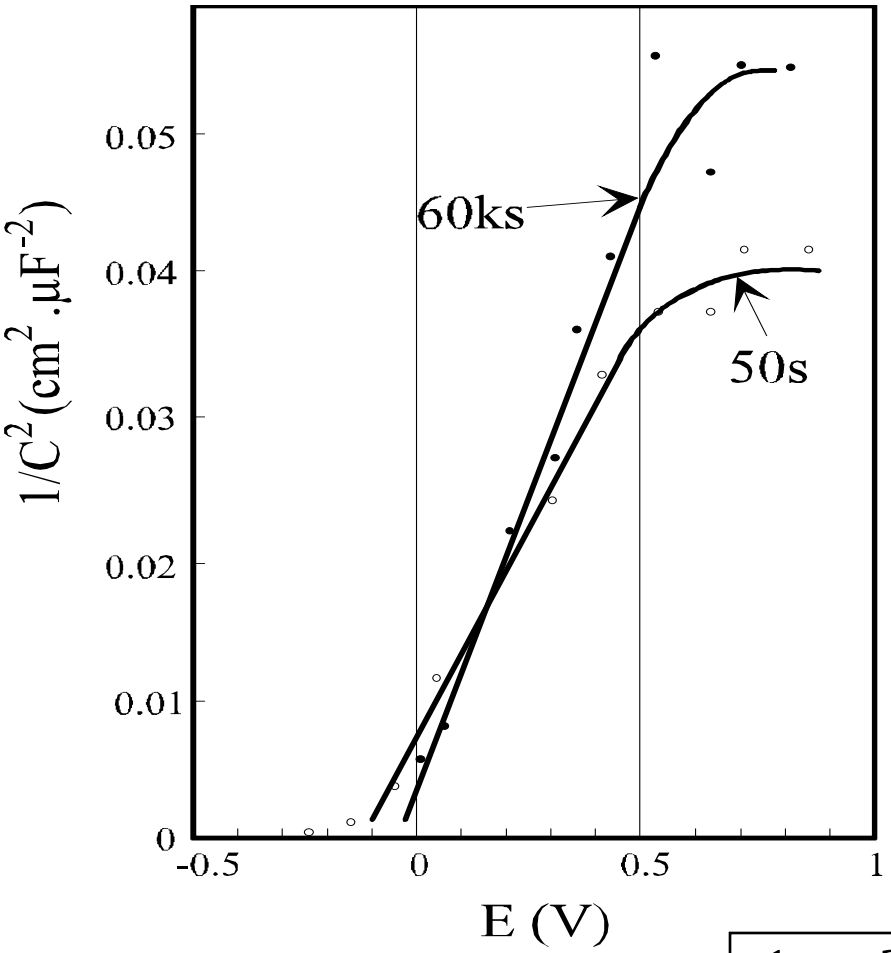

# Other Instances of M.S. behaviour (1)

$$\frac{1}{C^2} = (V - V_0)\frac{2}{N\varepsilon kT}$$

M.S. Diagram obtained on a mechanically polished AISI430 type steel, in deaerated NaCl (0.02M) pH6.6 after polarising 16h at +200mV/SCE.

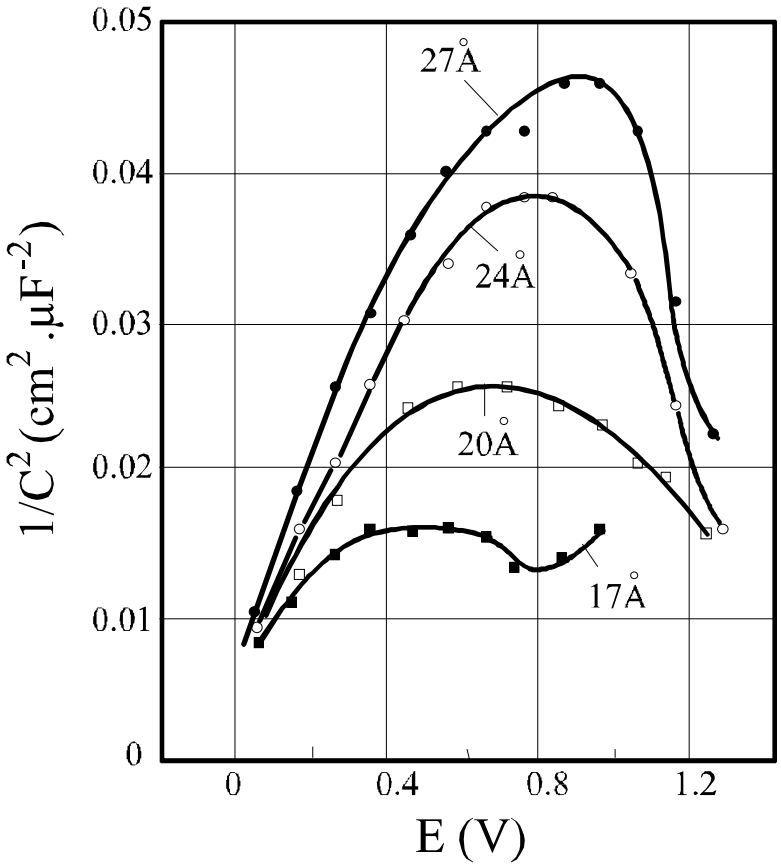
Impedance was measured using several frequencies: The frequency dispersion reflects the time needed for the trapping-detrapping process

# Other Instances of M.S. behaviour (2,3)

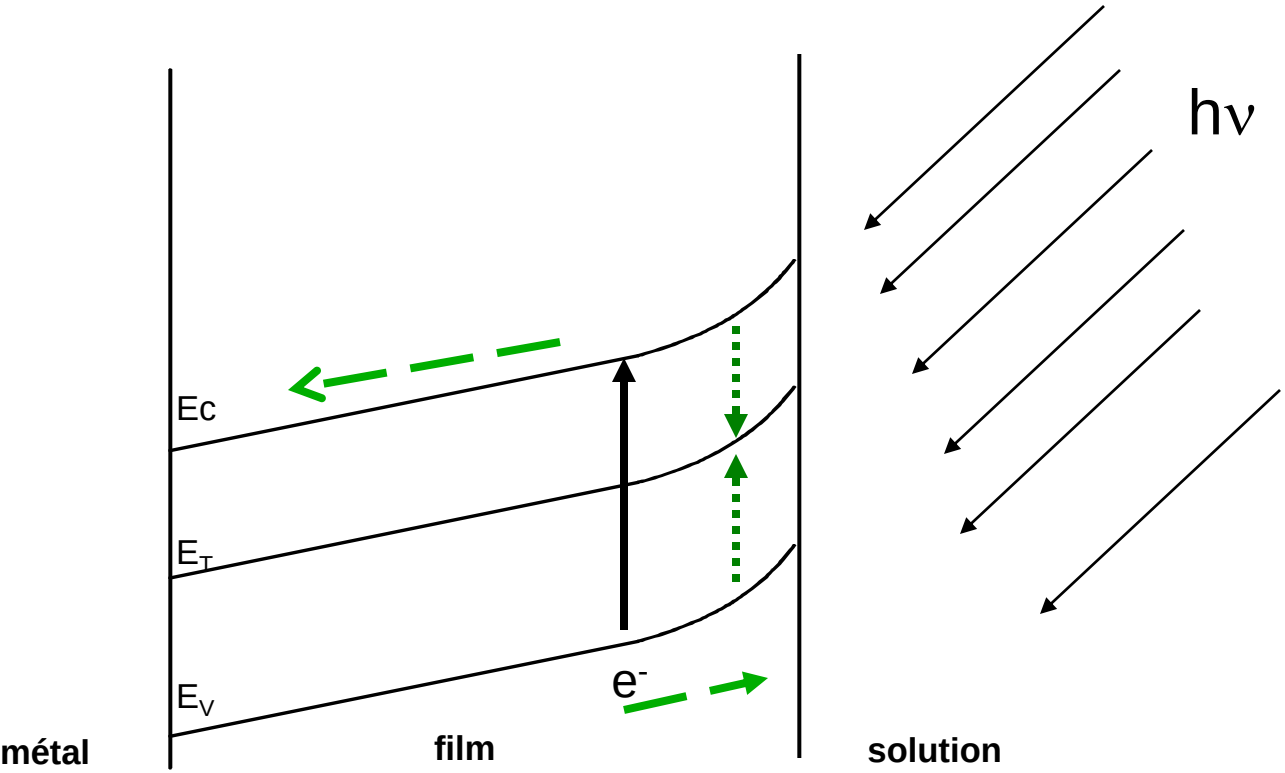



Effect of the polarisation time

$$\frac{1}{C^2} = \frac{2(V_0 - V)}{N\varepsilon kT}$$




Effect of the film thickness



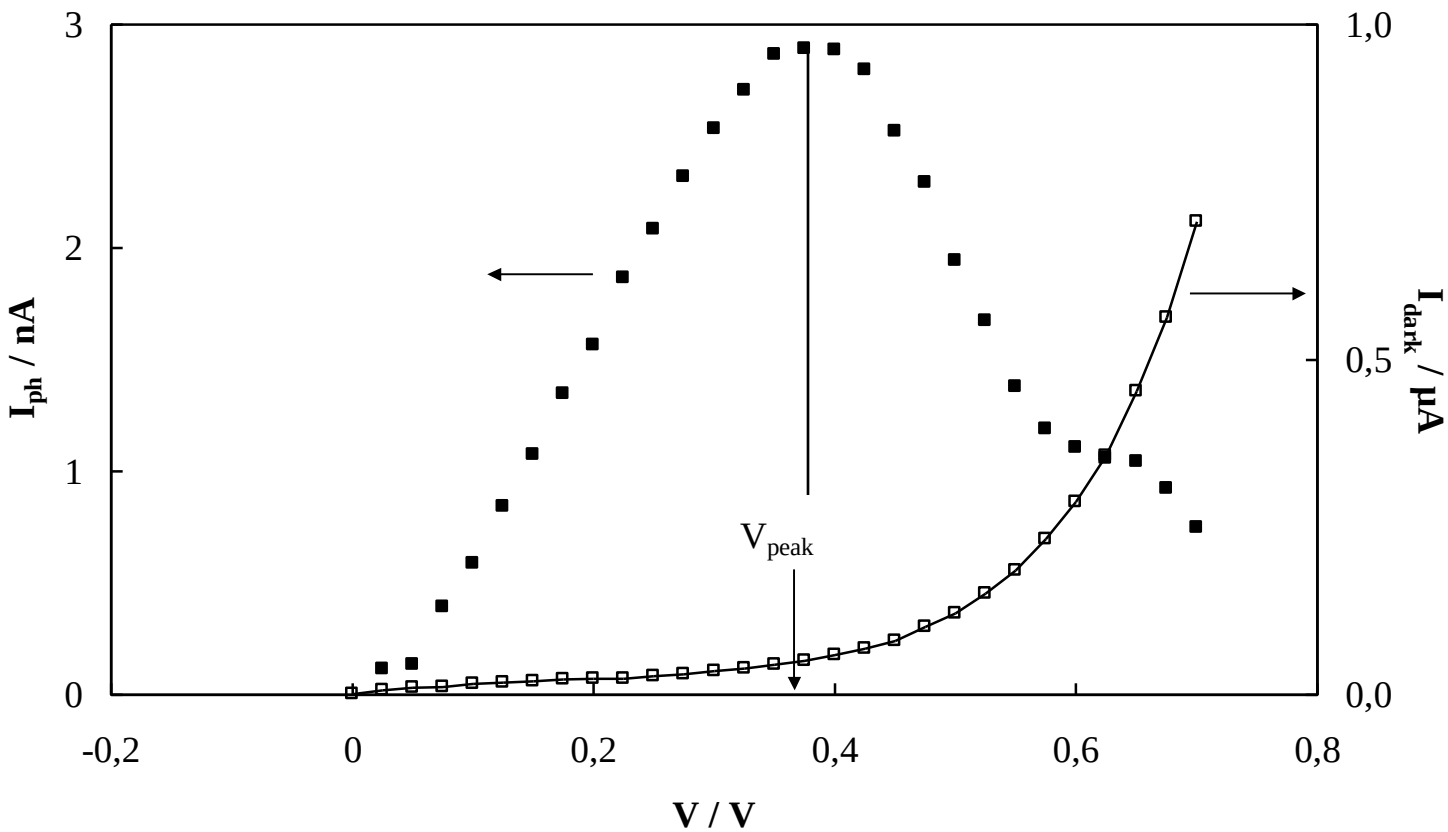

# Photo-electrochemical effects

**Formation of an electron hole pair**

**Pair anihilation : recombination on an electron trap energy level**

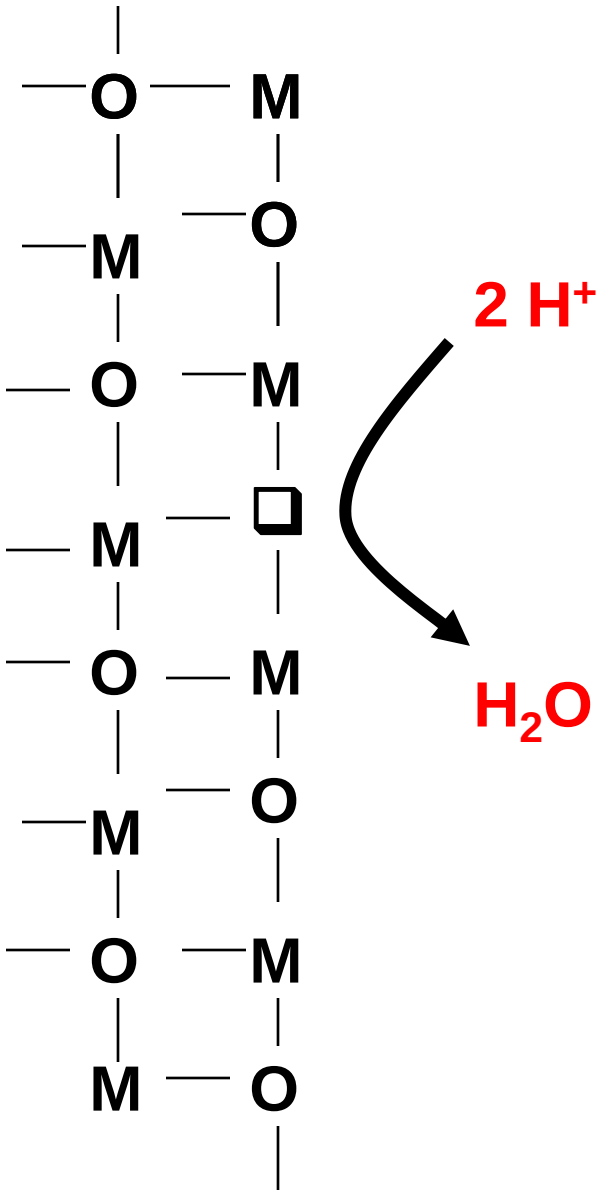
**photocurrent**

# An instance of PEC response of passive films




Potential dependence of the photocurrent (■) and dark current (□) for a passive film formed in NaCl 0.02mol.dm$^{-3}$ , Ar10%$H_2$ ($t_p$=15h30), $pH_f$ = 3.0. Experimental conditions: pHm = 5.2, sweep rate 0.1V/120s. l=501.7nm, P=60mW.cm-2, light modulation frequency 45Hz.

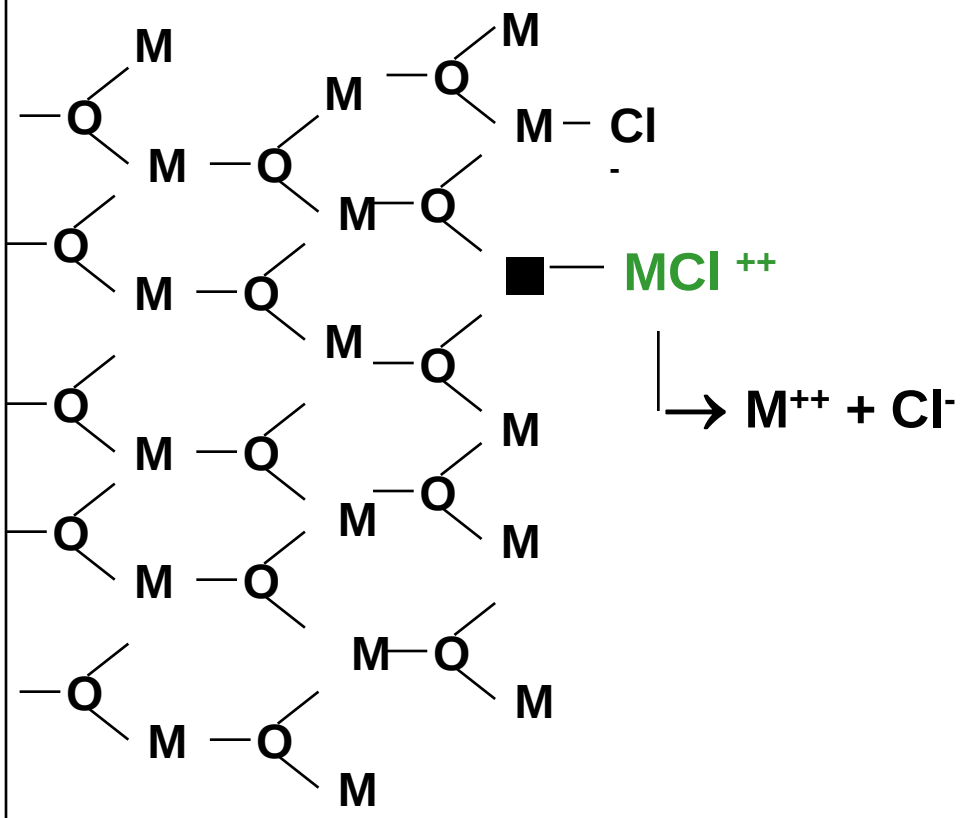
# Corrosion of passive films: The acidic attack




- The first step of acidic attack results in the net transfer of a negative charge ($O^{--}$) from the film to the environment.
- **The reaction rate is then expected to decrease when the electrode potential increases**
- When the $O^{-}$ vacancies are in a sufficient amount, the cationic bond is weakened leading to the film dissolution
- **This corrosion is expected to be uniform on all the surface**

## Corrosion in chloride containing electrolytes:

## The vacancy Injection process

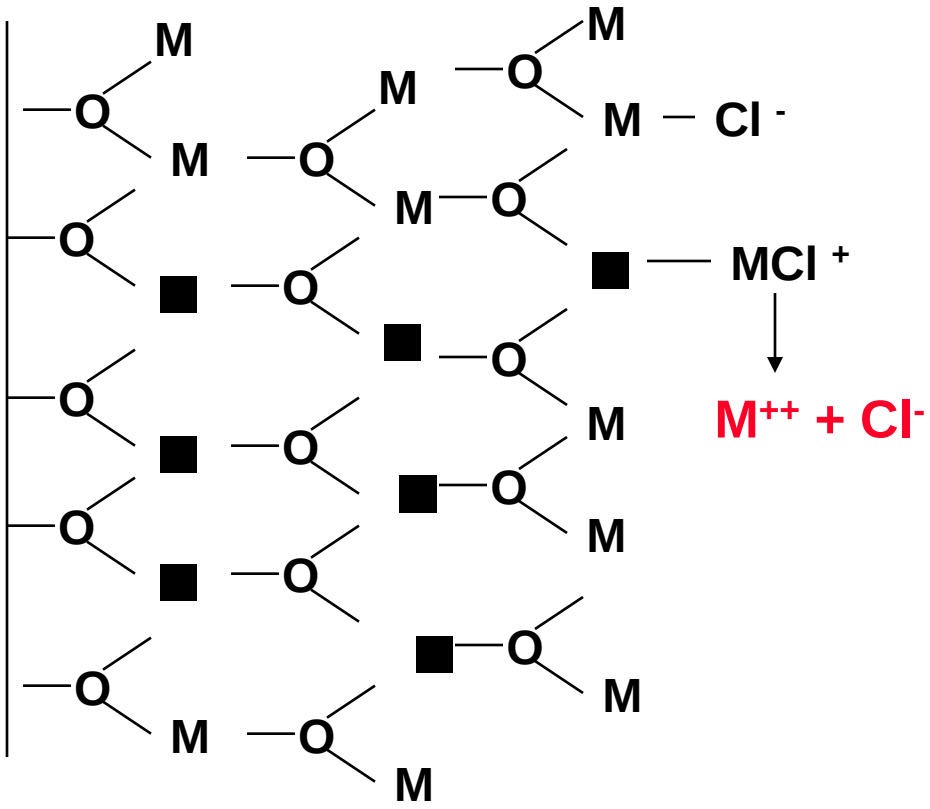


**1) Choride ions favours the action dissolution et the atomic scale, creating cation vacancies inside the film.**

**2) Under the effect of the electric field,** cation vacancies migrates toward the metal/film interface, where they eliminate proportionally to their concentration ⇒ $dX/dt = J - K.X$ leading to the stationnary concentration $X = J/K$

# Destabilising effect of cation vacancies

***(Role of the Chloride ions)***




**1) Choride ions favours the action dissolution et the atomic scale, creating cation vacancies inside the film.**

**2) Under the effect of the electric field,** these vacancies migrate toward the metal/film interface, where they eliminate proportionally to their concentration ⇒ **$dX/dt = J - K.X$** leading to **the stationnary concentration $X = J/K$**

**3) <u>When the vacancy</u> concentration increases , the passive film cohesion decreases. At a critical value $X_{crit}$ the film may locally break down .**

**4) <u>Electrostriction theory</u>: When the cohesion forces do not counterbalance the electrostriction forces, «local» film breakdown may occur** *(cf. N.Sato) .*

**NB: The mechanical breakdown should release the mechanical stresses around the breakdown point. This form of corrosion is then expected to be localized**

# The Pit nucleation potential

**1) The vacancies creation rate J increases with the solution chloride content and electrode potential :**

$$J = cst.c^n.\exp V_{fs}/\phi = cst.c^n.\ \exp (1-\gamma)V_E/\phi$$

where $\gamma = dV_f/dV_E$ is a share coefficient

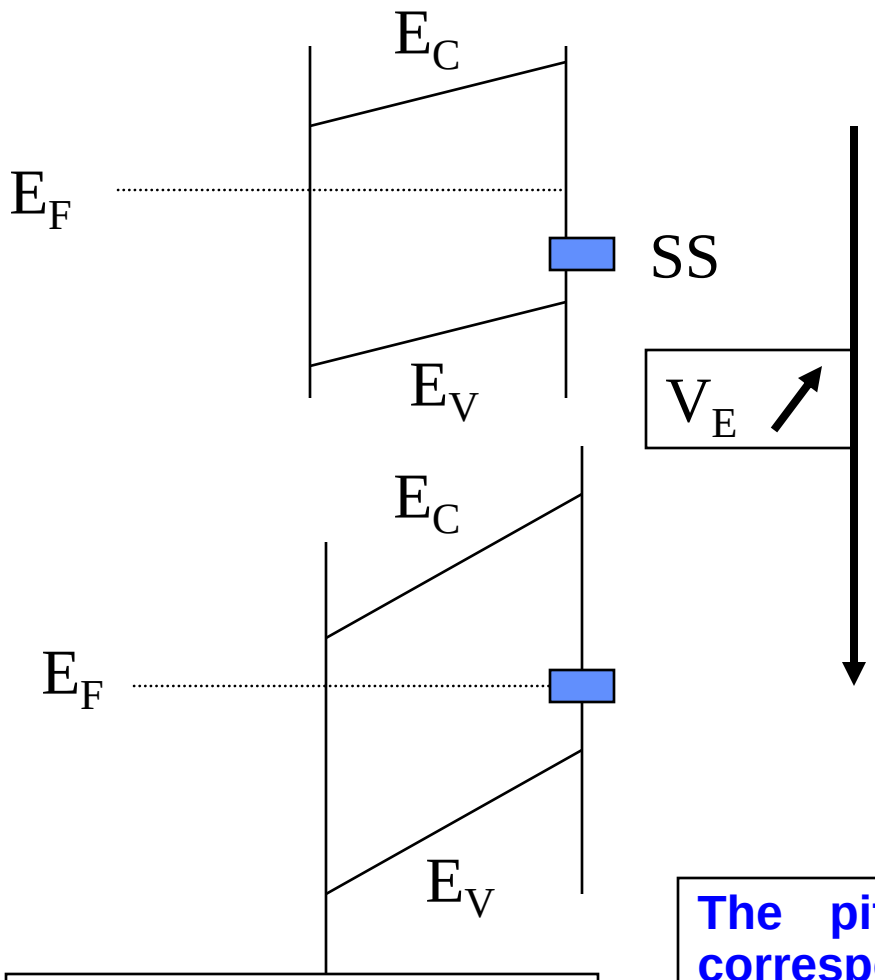
**2) A pit nucleation potential may be defined as:**

$$J(C,V_{pit}) = KX_{crit}$$

**It decreases when the chloride concentration increases**

# The Pit Nucleation potential (details)

$V_E < Vpit \Leftrightarrow Ess < E_F$




$V_E > Vpit \Leftrightarrow Ess = E_F$

## Below the pitting potential:

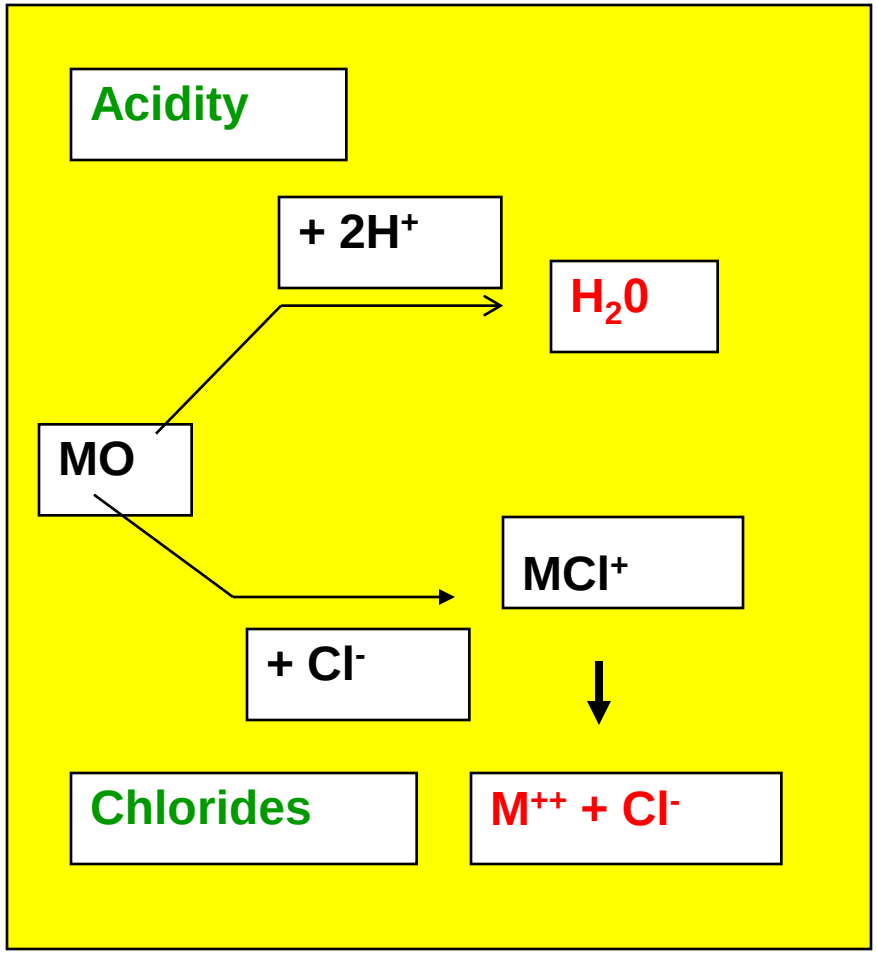
Any increase in electrode potential is concentrated inside the passive film. Then the potential drop at the outer interface keeps constant. The vacancy concentration in the film is negligible and does not depend on electrode potential

## Above the pitting potential:

The metal Fermi level is pinned on the electron surface states energy level. Then the potential drop within the film is constant and any increase in electrode potential concentrates at the film electrolyte interface. The vacancy concentration in the film quickly increases with electrode potential

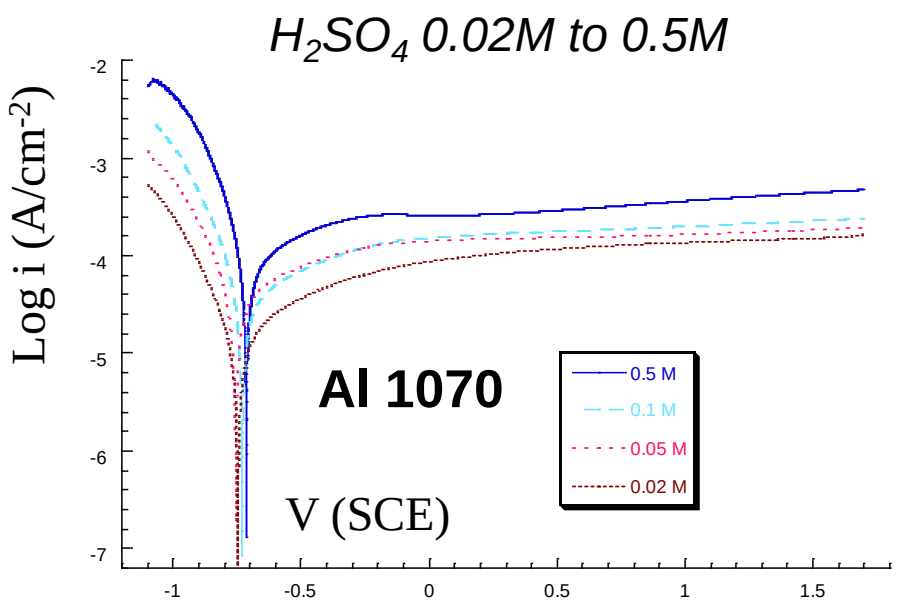
**The pit nucleation potential could simply correspond to the pinning of the Fermi level on an electron acceptor level present at the film solution interface.**

# Part III: Passivity breakdown

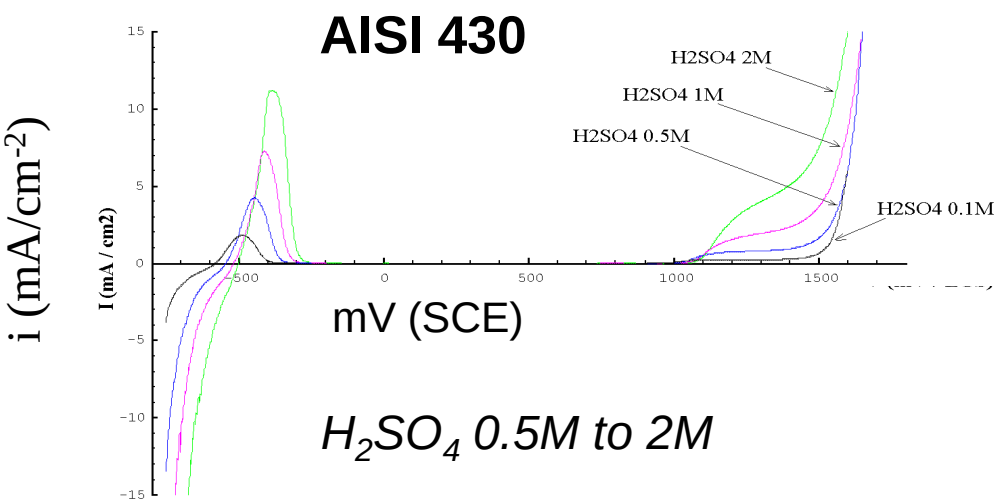



| CORROSION RISK | *Quasi-neutral* | *Acidic* |
|---|---|---|
| *Chloride free* | NO | UNIFORM CORROSION |
| *Chloride containing* | LOCALISED CORROSION | HAZARD!! |

# Polarisation curves
## *in acidic media*




Aluminium alloys




Stainless steels

# Modelling the polarisation curve *(1)*

| | | |
|---|---|---|
| Passivation: | $M+H_2O \leftrightarrow MO + 2H^+ + 2e^-$ | (1) |
| Dissolution: | $M \rightarrow M^{++} + 2e^-$ | (2) |

Fraction passivée (recouverte par MO) = $\theta$

Activité du proton en surface $\propto$ $\xi = H^+ \exp - \frac{qV}{kT}$

Loi d'action de masse (1) : $1 - \theta \propto \theta\, \xi^2 = \theta\, I u^2$ avec:

$$\boxed{u = \xi_{1/2} / \xi = \left[\xi_{1/2} / H^+\right] \exp \frac{qV}{kT}} \quad \Rightarrow \exp \frac{qV}{kT} \propto u.H^+ / \xi_{1/2}$$

$$\theta = \frac{u^2}{1+u^2}$$

= 0 pour les potentiels cathodiques et/ou les milieux acides

= 1 pour les potentiels anodiques et/ou les milieux basiques

Loi cinétique (2) (Tafel) :

$$\boxed{i \propto [1-\theta] \exp \frac{\beta qV}{kT} \propto \left[H^+\right]^\beta \frac{u^\beta}{1+u^2}}$$

# Modelling the polarisation curve *(2)*

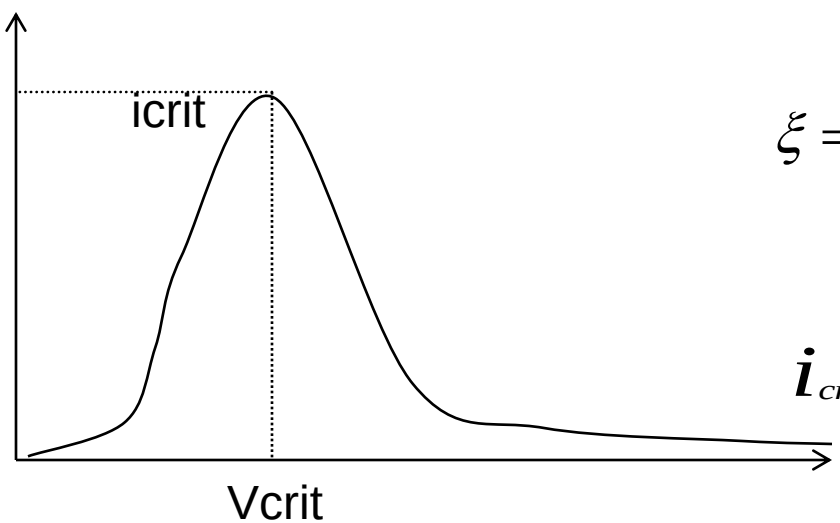
$$\boxed{i \propto [1-\theta]\exp\frac{\beta qV}{kT} \propto [H^+]^\beta \frac{u^\beta}{1+u^2}}$$ avec $$u = [\xi_{1/2} / H^+]\exp\frac{qV}{kT}$$

Qui varie comme $u^\beta$ pour les potentiels cathodiques et/ou les milieux acides

Qui varie comme $u^{\beta-2}$ pour les potentiels anodiques et/ou les milieux basiques

Si $\beta < 2$ , cette fonction présente un maximum $i_{crit}$ pour $u=u_{crit}$, $V=V_{crit}$ , avec:

$u_{crit}^2 = \beta/(2-\beta)$ ($\Rightarrow \theta = \beta/2$) . Il en résulte que:




(1) $V_{crit}$ suit une loi Nersnstienne :

$$\xi = H^+ \exp -\frac{qV_{crit}}{kT} = \xi_{crit} = \xi_{1/2}/[\beta/(2-\beta)]^{1/2}$$

(2) $i_{crit}$ décroit linéairement avec le pH :

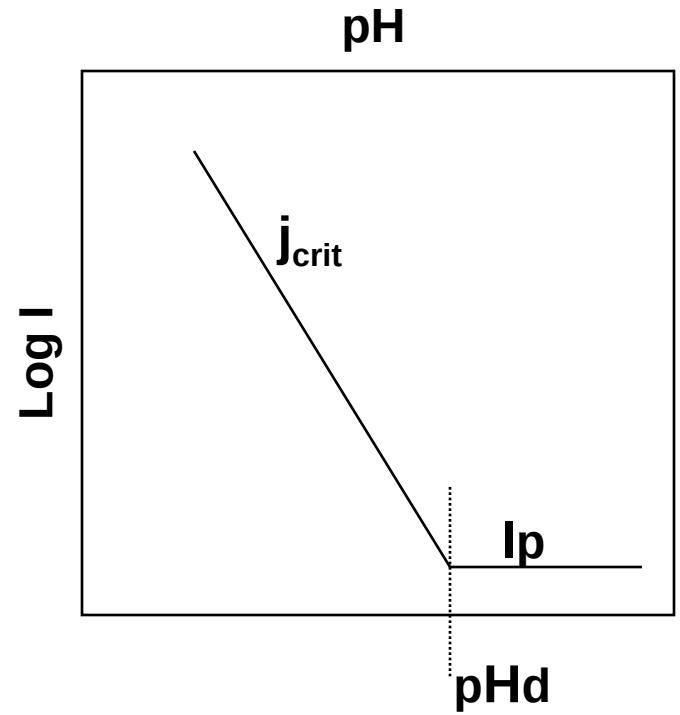
$$i_{crit} \propto [H^+]^\beta$$

$$\boxed{\Rightarrow \log i_{crit} = \text{cst.} - \beta.\text{pH}}$$

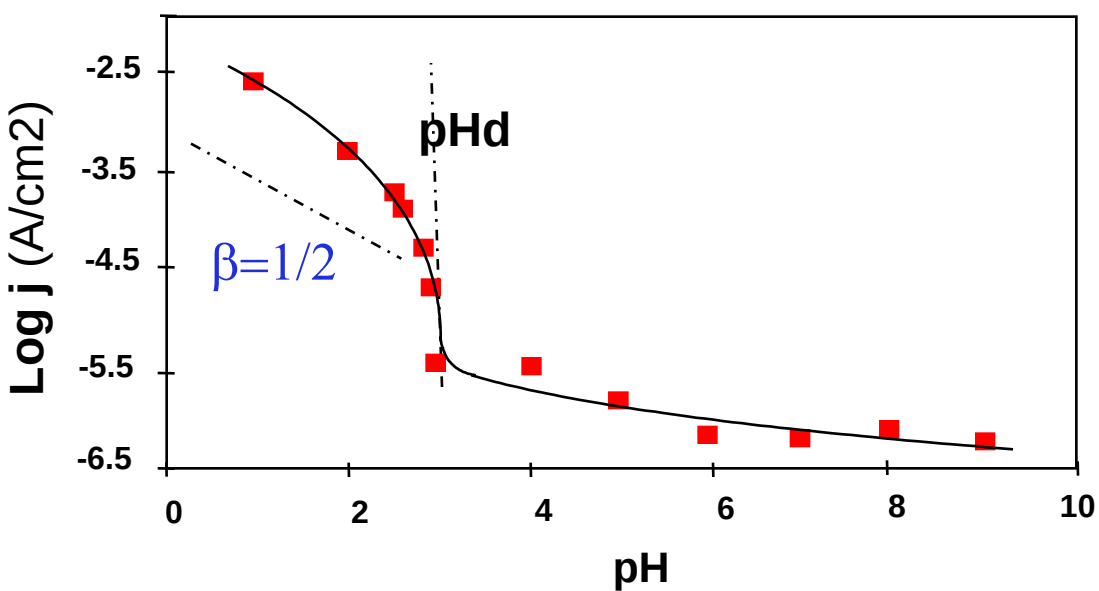
# pH effect *(Stainless steels)*

$V_{crit}$ = cst. +2.3kT/q pH (Nernst)

And **log $j_{crit}$ = cst. - β.pH**




*(430 Ti in deaerated Na2SO4 1M)*




**Theory**

**Experience**

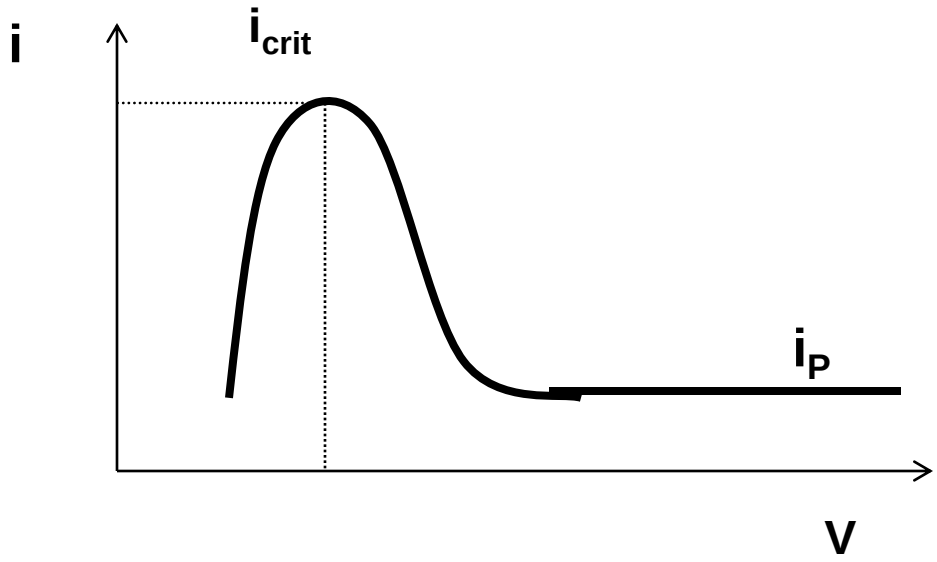
# Polarisation Curve *(general)*

Le courant global **i** est la somme de 3 courants partiels:

1) Le courant de dissolution anodique $i_A$

2) Le courant sur les sites oxydes, proportionnel a $\theta$ et tendant vers une constante $i_P$ lorsque $\theta$ tend vers 1

3) Le courant cathodique $i_K$

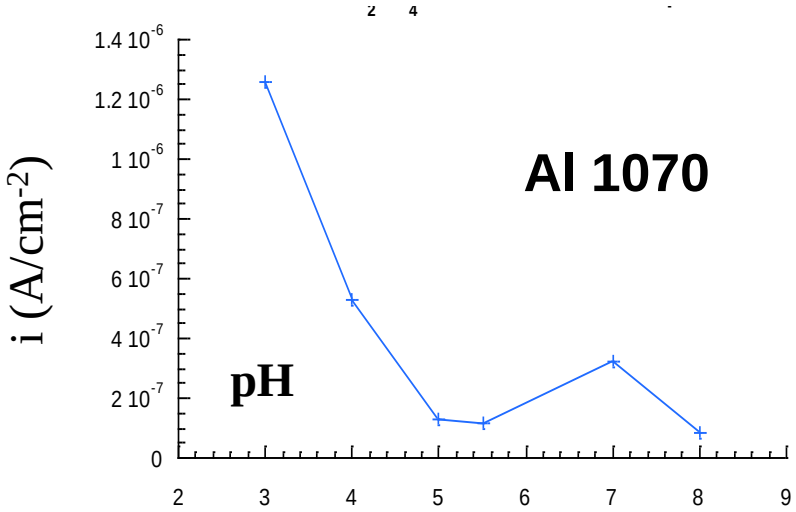



Passivité de type

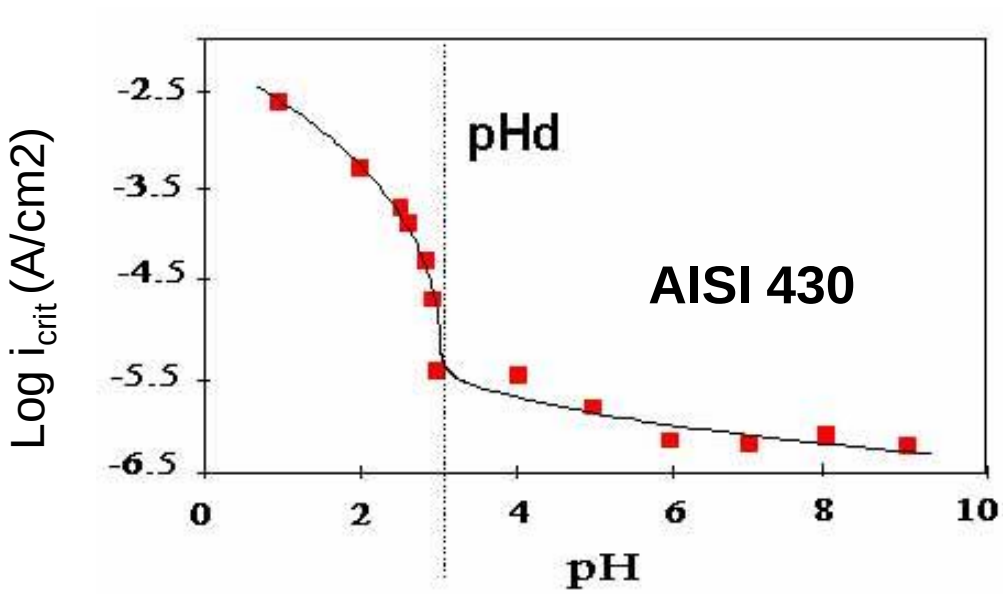
Fer, Cr, S.S. $i_P << i_{crit}$

Al : $i_P > i_{crit}$

Corrosion current in acidified Na2SO4



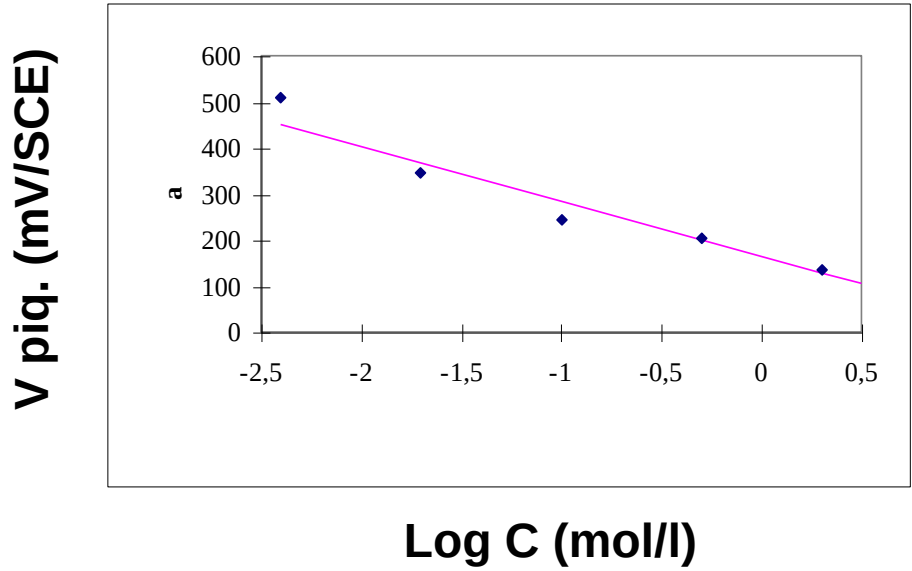

**Depassivation pH**

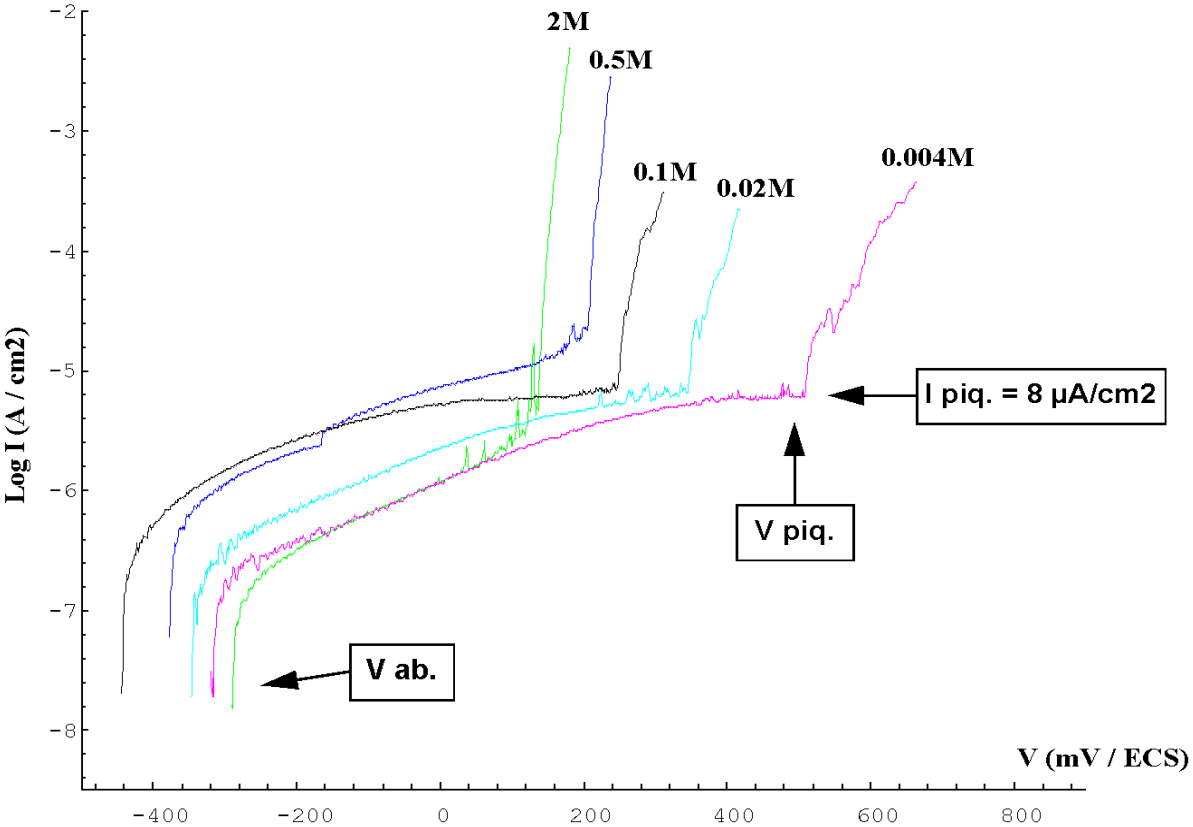



critical passivation current in acidified Na2SO4

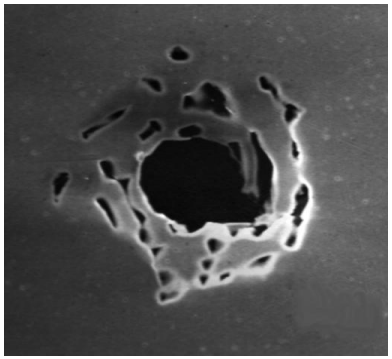
# Behaviour of S.S. in neutral chloride containing media: the pitting Corrosion

*(430 Ti in deaerated NaCl pH6.6)*



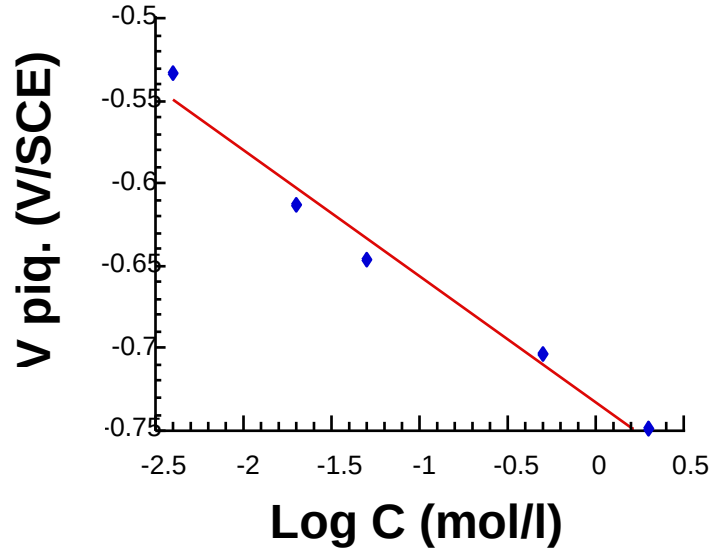



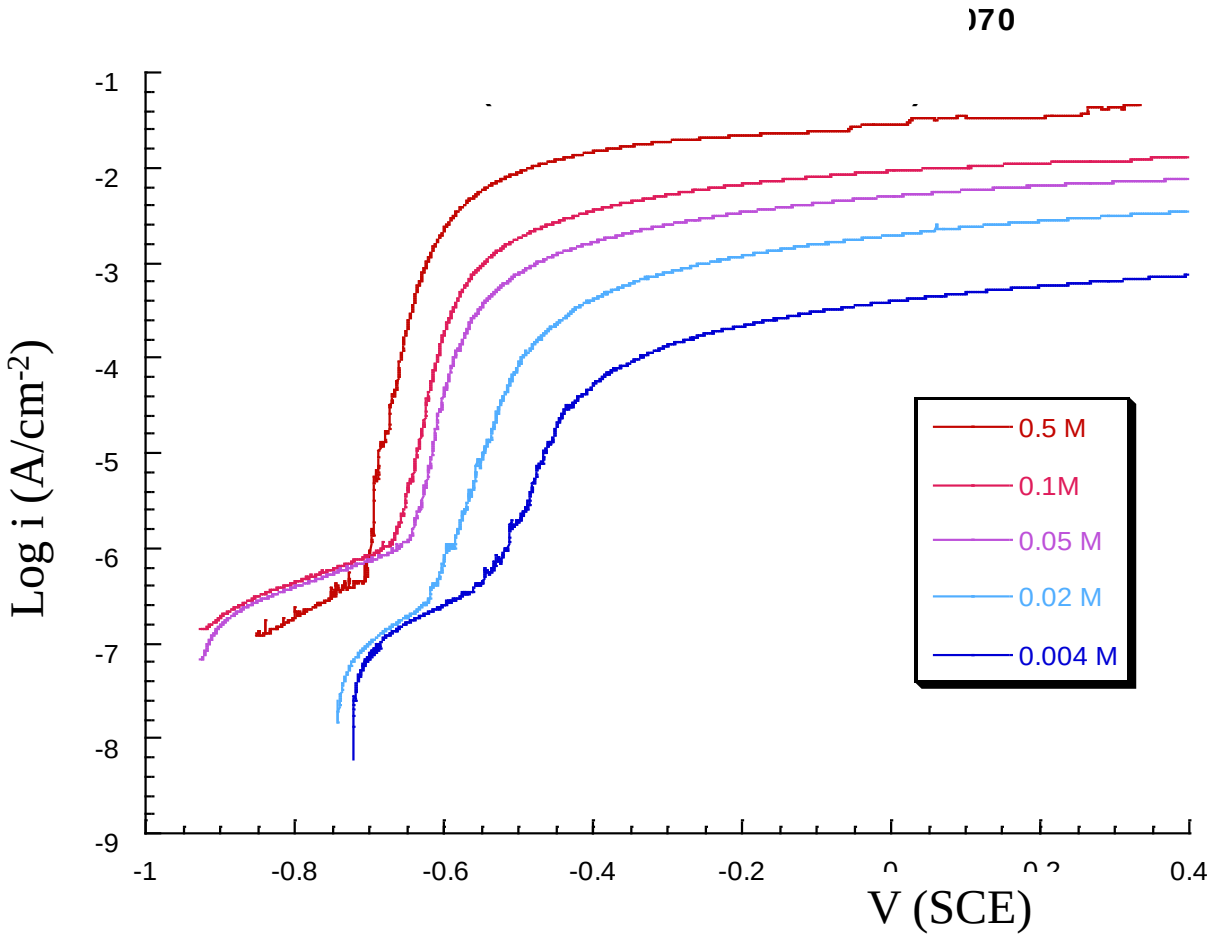

**The pitting potential** decreases when increasing the Chloride content



# Behaviour of Al in neutral chloride containing media

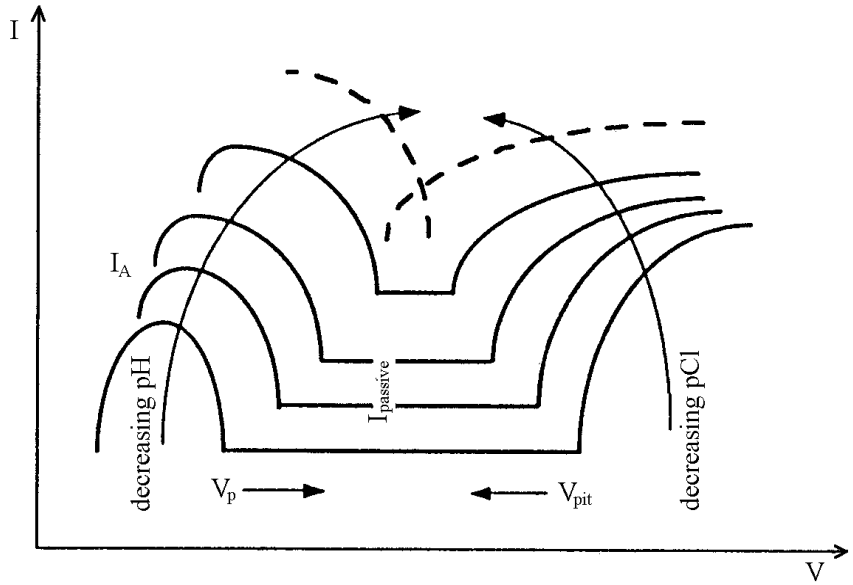
*(Al1070 in deaerated NaCl pH6.6)*




As for Stainless steels, The pitting potential diminishes linearly with the logarithm of the chloride content.

# The Corrosion risk in chloride containing acidic media

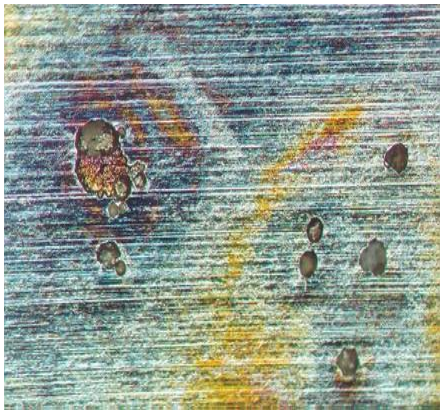


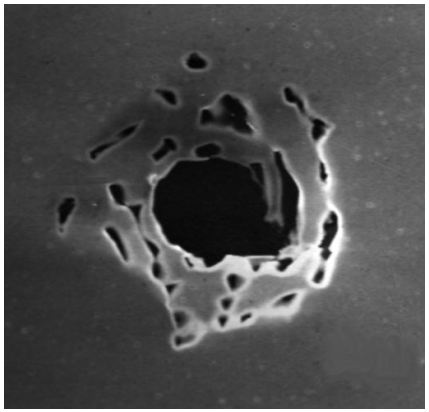

- The fall in pH and the increase in the $Cl^-$ content reduces the passive range

# The successive stages of localised corrosion

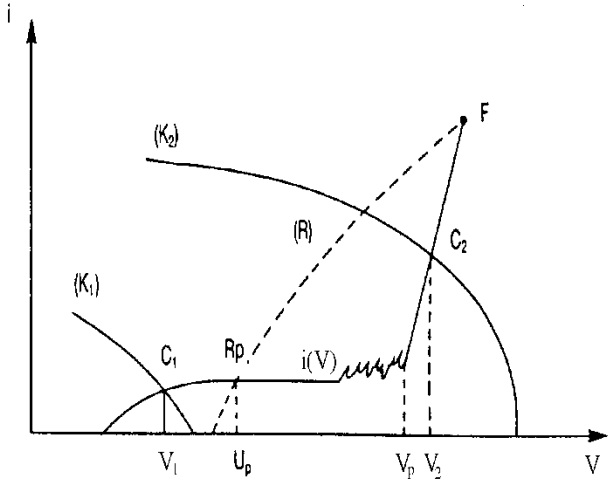
- **Initiation**
  - **The generic modes** *(Pitting, Crevice,SCC…)*
  - **Environment effects** *(Marine, atmospheric, MIC…)*
  - **Effect of the material** *(specific)*
- **Propagation** *(common mode)*
  - **Chloride enrichment**
  - **Hydrolysis of dissolved cations**
  - **High propagation rate**

# Pitting Corrosion
## in neutral chloride containing media





(AISI 304)




The pitting potential is an appropriate criterion for pitting corrosion resistance

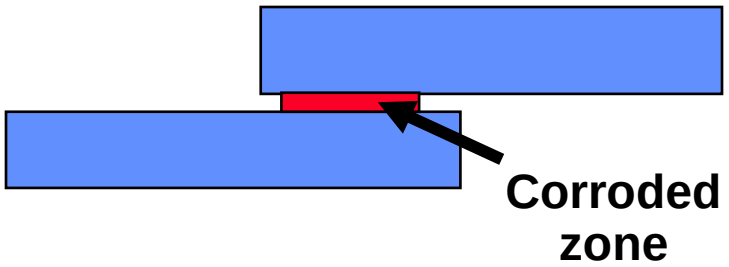
## The successive steps of pitting corrosion

- **Pit nucleation** (nanometric scale)
  *Local passive film breakdown.*

- **Metastable pitting** (micrometric scale)
  *Possible repassivation, current transients.*

- **Irreversible damage** (milimetric scale)
  *Pit propagation*

# Crevice corrosion?




## What happens in a crevice?

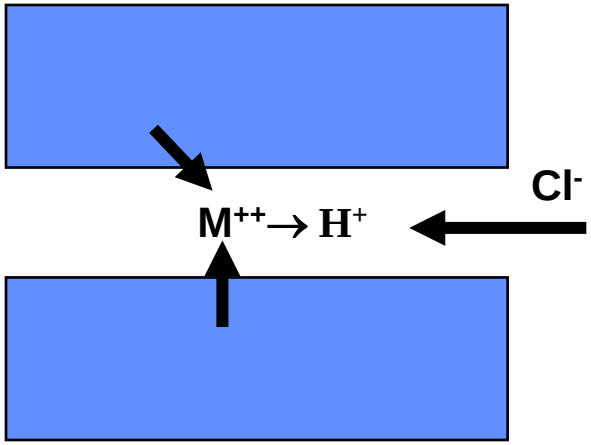
**1) Cathodic reaction** quickly exhaust oxygen in the crevice. Further cathodic reaction occurs then outside

**2) Anodic dissolution** across the passive surface, leads to an enrichment in dissolved cations

**3)Chloride enrichment :** Influx of the majority anion to compensate for the positive charges (electromigration)

**4) Hydrolysis of cations (⇒ Hydrochloric acidity)**

limited by the migration and the diffusion of reaction products outside the zone.




## The remedies:

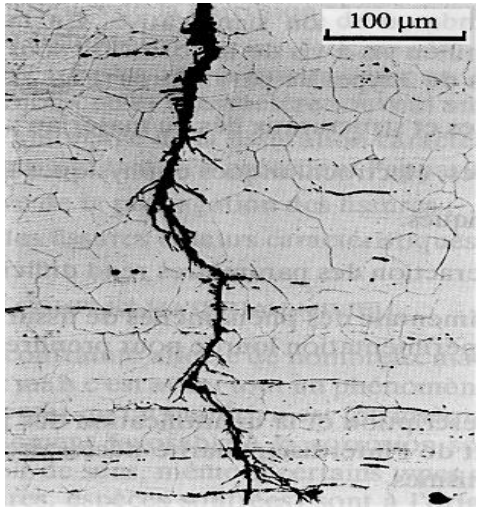
**1) Material selection** (for a “sufficient” resistance to acidic corrosion)

**2) To avoid crevices!**

# Mechanical Effects

## The Detrimental effect of Stress …


- **Stress corrosion cracking**
- **Corrosion-Fatigue**
- **Fretting Corrosion …etc…**




## Stress corrosion cracking

**Conditions of occurrence:**
hot chloride containing environment.

**Remedy:** selection of appropriate grades. For instance, the use of austeno-ferritic or ferritic steels is preferable to FeCrNi austenitic steels.

**The association of mechanical stress and corrosive conditions:**
may lead to damage which neither the mechanical stress nor the corrosion would have caused separately.

**Optical microscopy**

crack propagation rate

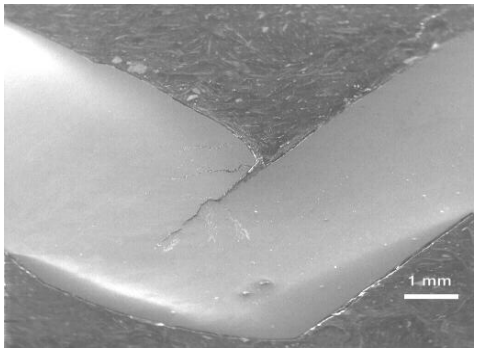
# SCC facies

**SEM** Transgranular cracking

30 µm

Cracks in stainless steels can either be intergranular or transgranular or sometimes mixed.

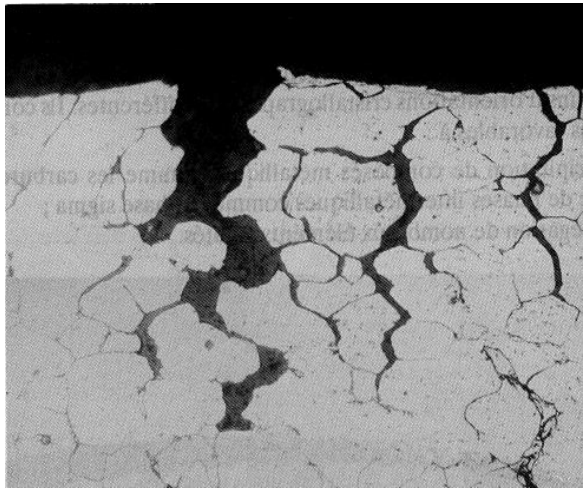
Transgranular cracks often show continuous striations, perpendicular to the crack growth direction, which are generally considered to mark successive stages of propagation (discontinuous propagation rate).

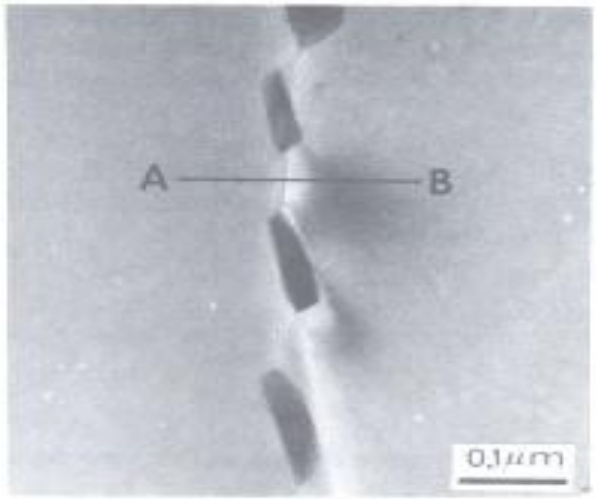


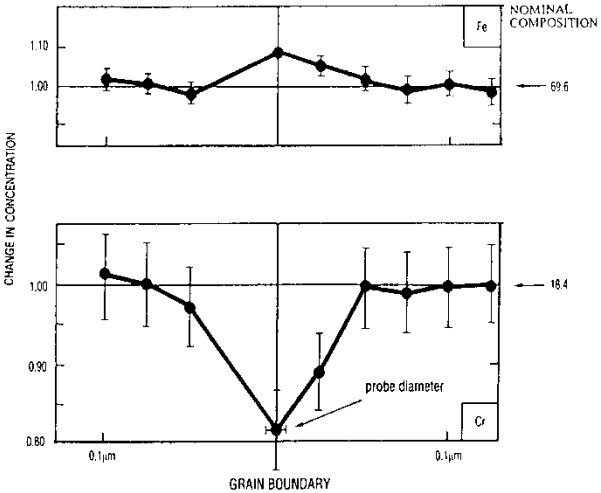

*Effect of residual stresses*

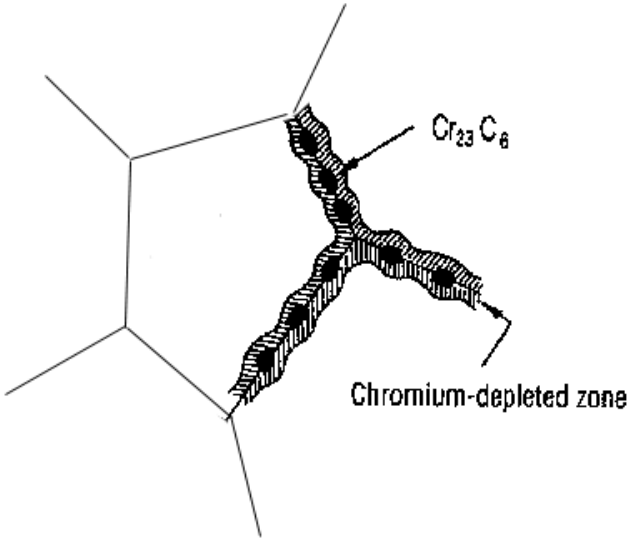
# IV) Metalurgical effects

## Intergranular Corrosion of stainless steels:
## Carbide Precipitation and Chromium depletion



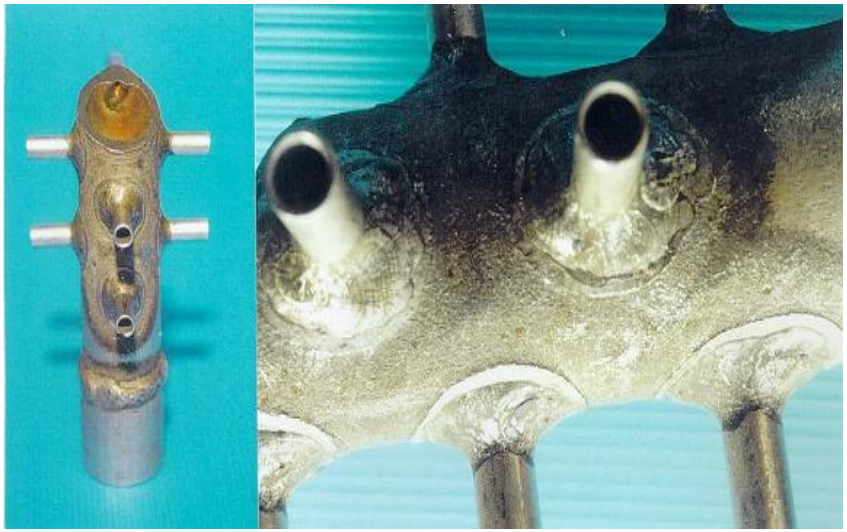


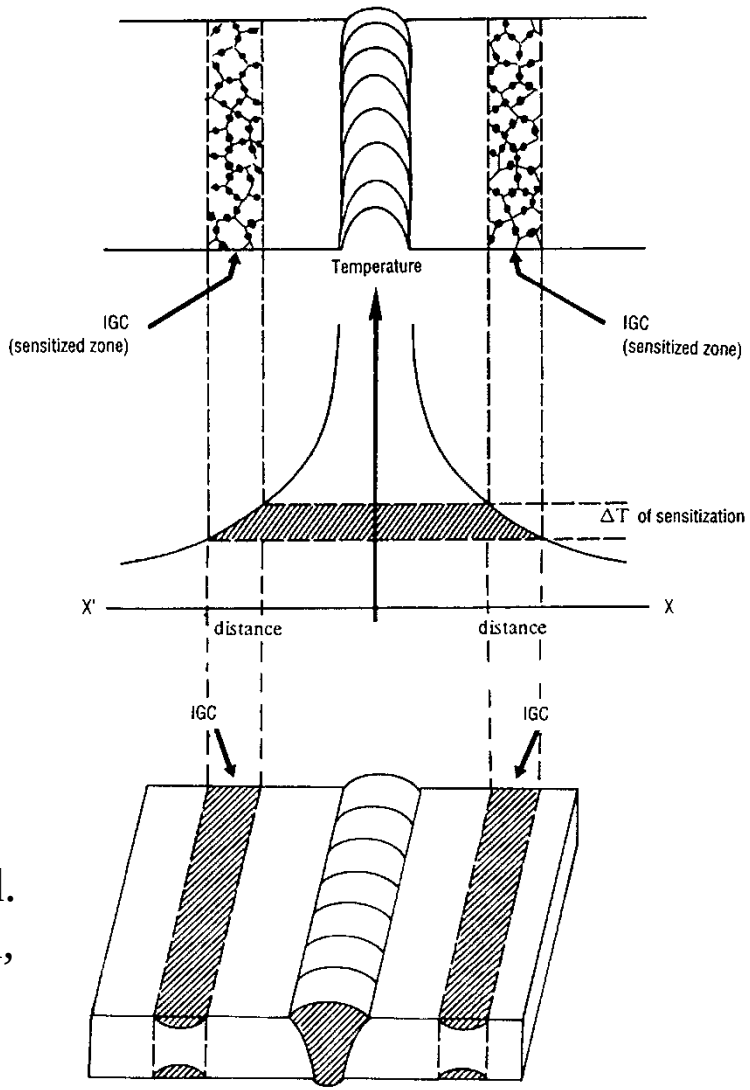




Chromium depletion in the vicinity of a grain boundary in an austenitic steel:
a) transmission electron microscope image
b) corresponding iron and chrornium concentration profiles..

# Heat Affected Zone close to the weldments






Example: Several secondary tubes are welded on a main tube. No post welding treatment was performed. Welds were then sensitised to intergranular corrosion, due to intergranular precipitation of chromium carbides in the heat affected zones.
The corrosion looks locally « uniform » all around the tube weldments

# IGC: The remedies

## Austenitic Steels

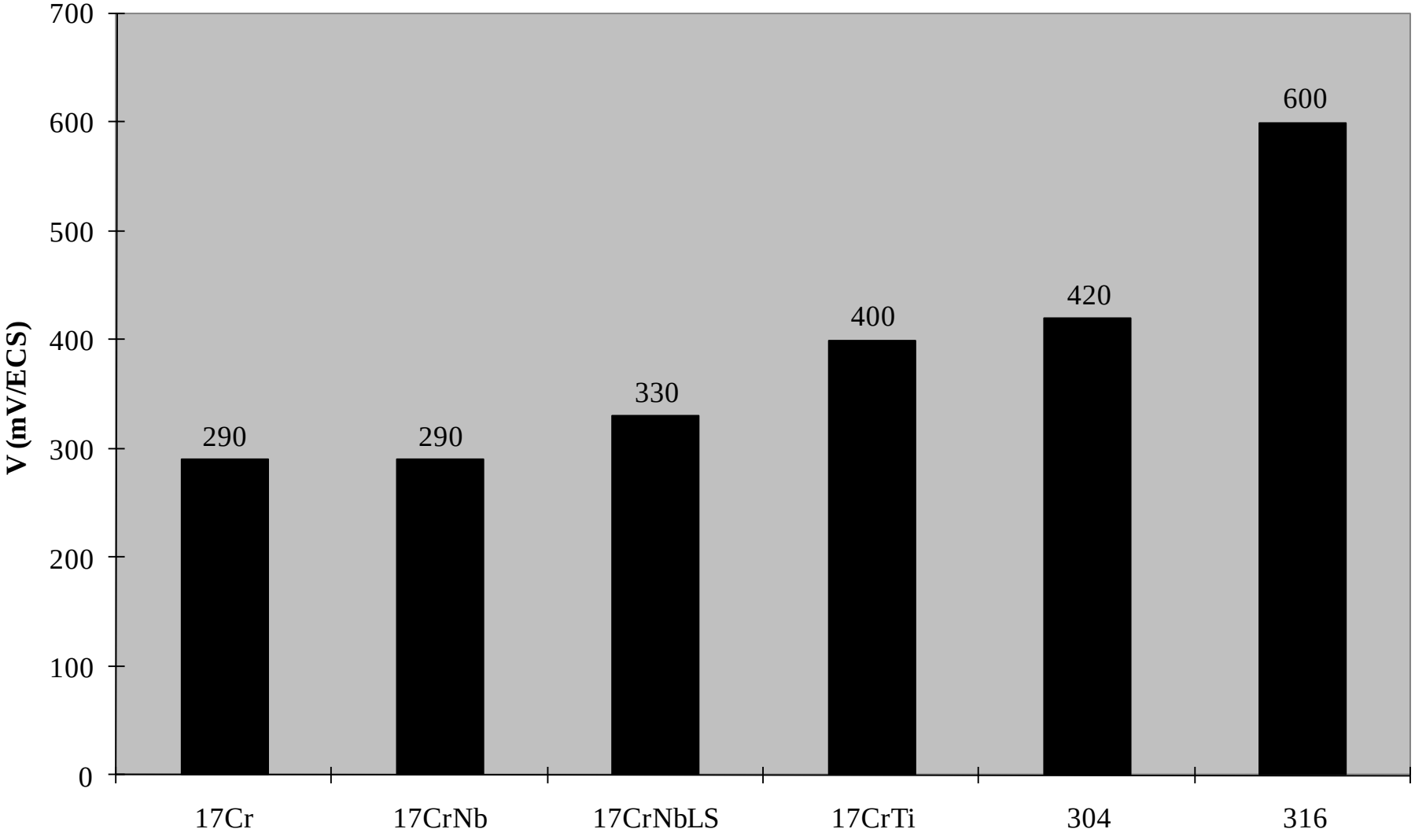
- Heat Treatments
  - solution treatment
  - annealing after welding (rarely used)
- Low Carbon Steels: C<0.03%
  - (304L, 316L , etc ..)
- Stabilised Steels
  - Stabilising elements : Ti, Nb, Zr.
  - Ex: Ti stabilised steel (grade 321) : Ti/C > 5 ? Maturation heat treatment

## Ferritic Steels

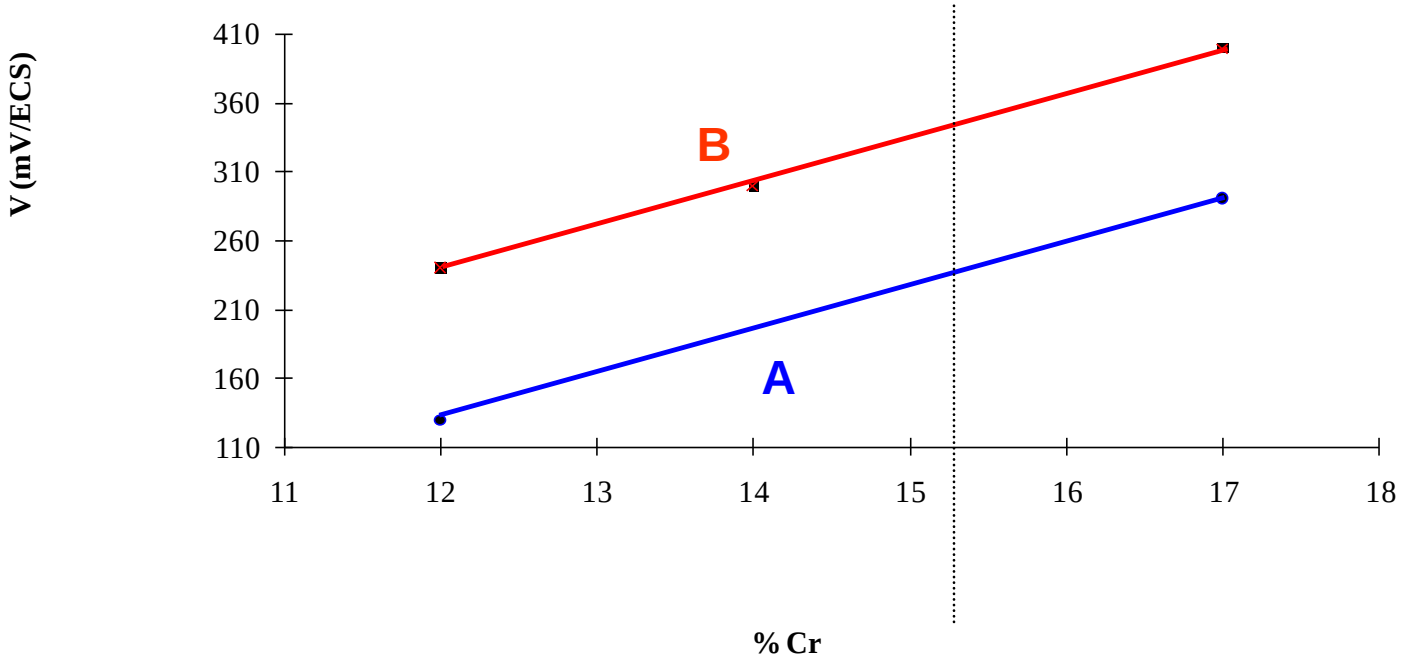
- Impossible solutions
  - Solution treatment
  - low carbon
- Possible solutions
  - annealing after welding
  - Stabilisation (Ti, Nb, Zr)
- Ex: Titanium stabilised steel
  - Ti>0.15% +4(C+N)
  - Other effect: sulfur trapping ⇒improvement of the pitting resistance

# Pitting potentials of stainless steels

*(In NaCl 0.02M)*



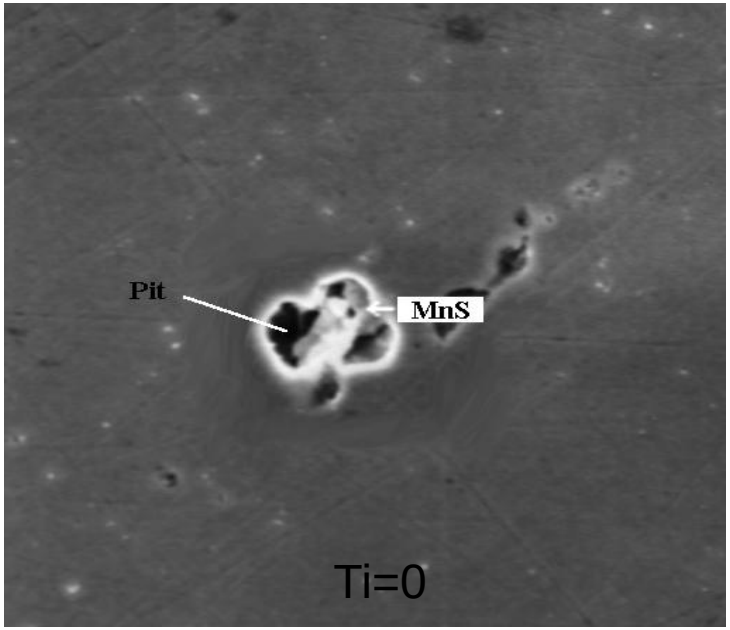
# Effect of the chromium content in an Fe - Cr alloy



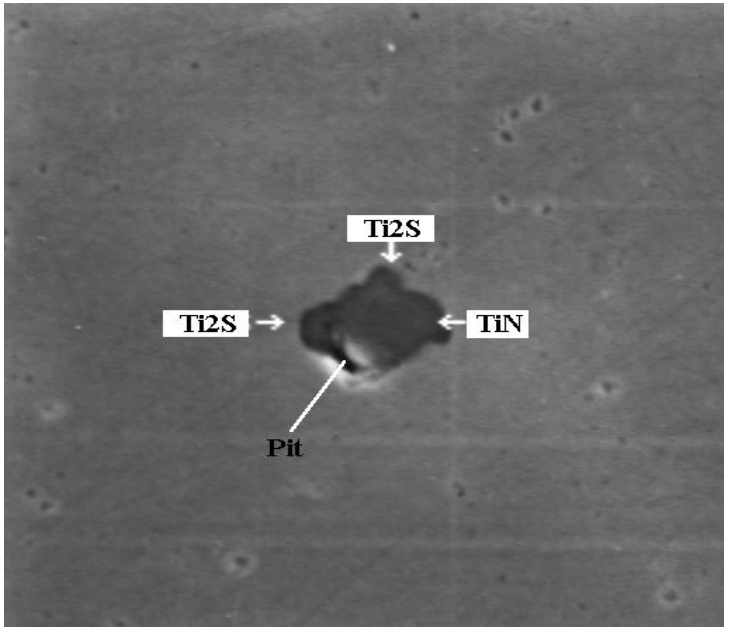

- **A: Steels with MnS (40 ppm S)**
- **B:Steels without MnS (+0,4%Ti)**

# Pitting on sulphide inclusions

Scanning electron microscopy (x 3000)




Pitting on a manganese sulphide



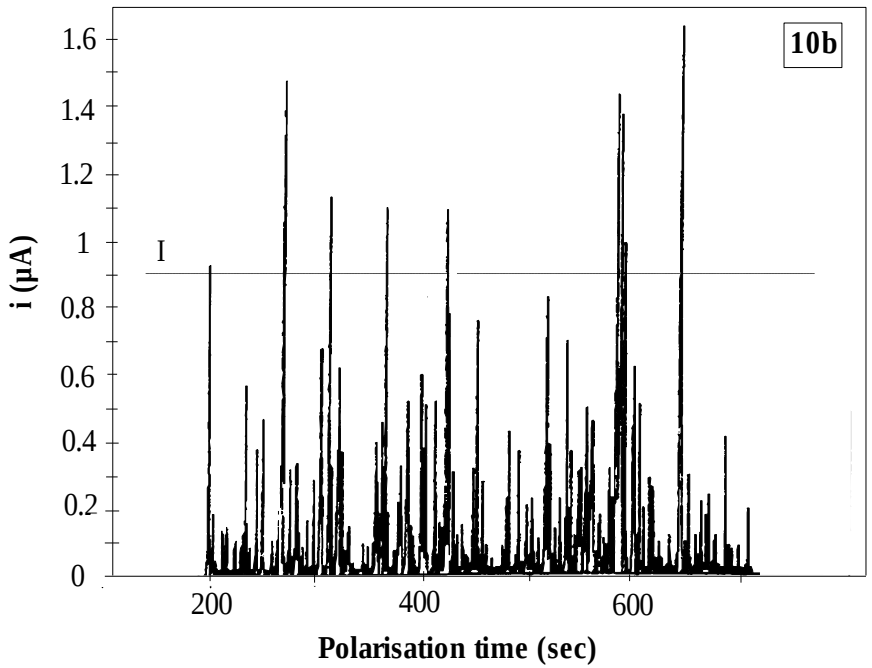

Ti=0.4%

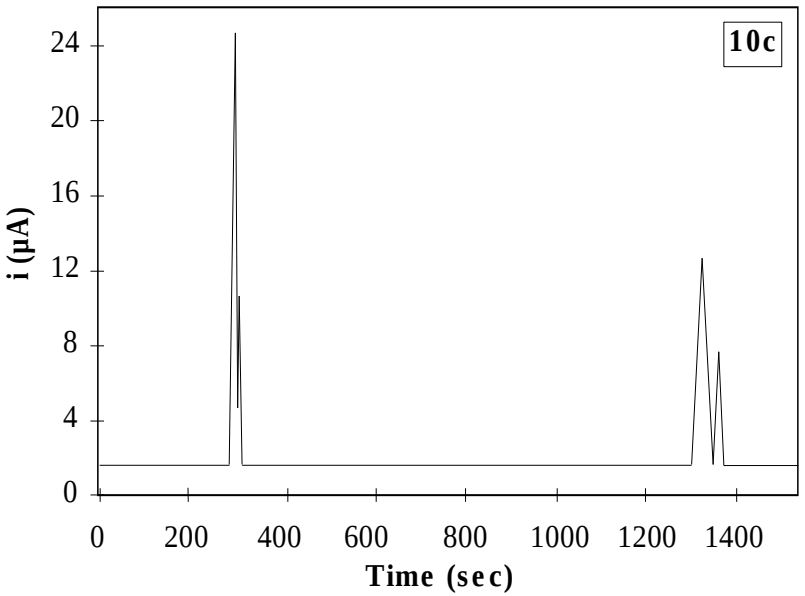
Pitting at the boundary of a Ti nitride

**Fe16Cr Mn=0.45% S= 40ppm**

# Prepitting events

during a polarisation at 200mV/SCE in NaCl 0.02M pH6.6



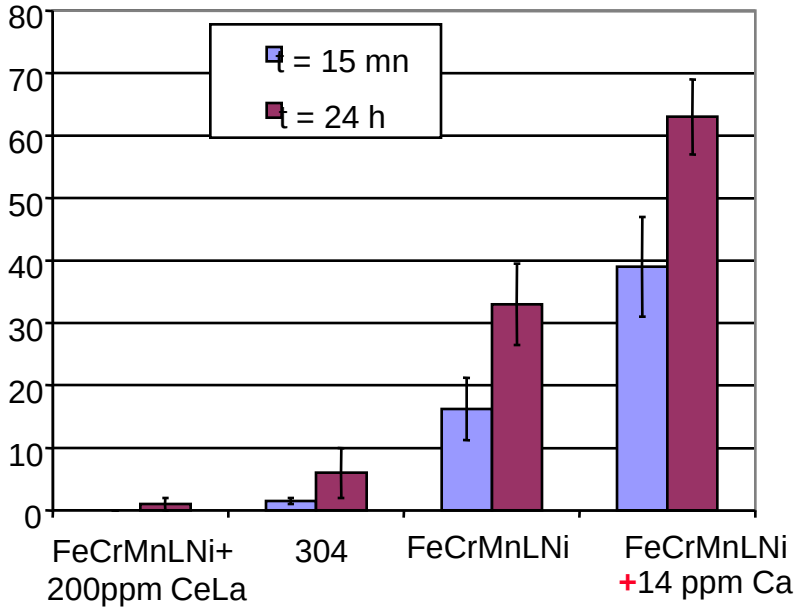




- *Left:* Typical anodic current variations for MnS containing steels.
- *Right:* Typical anodic micro-events for Ti bearing steels

# Effect of the sulfides solubility on the pitting potential

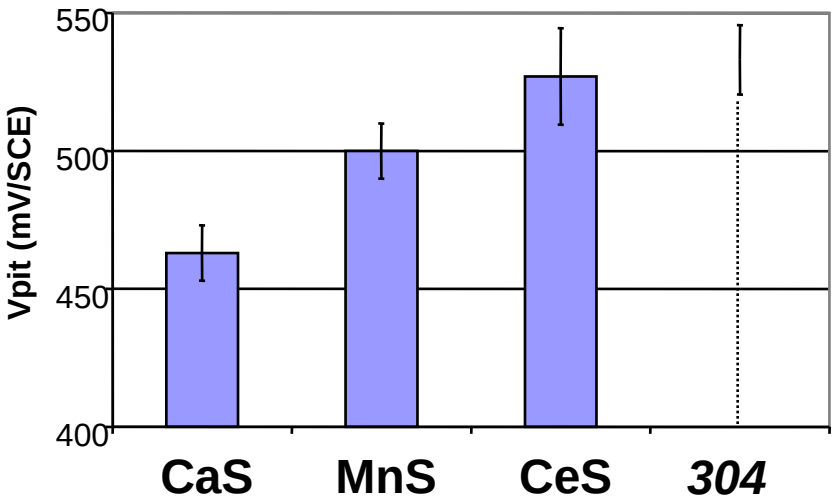
*In "Critical Factors in localized corrosion IV": Salt lake city 2002. The importance of being a metallurgist*

**% of dissolved inclusions after immersion in neutral 0.02M NaCl (observed by SEM)**




**CeS (Mn,Cr)S MnS CaS**

**Pitting potential**




| C % | Cr % | Ni % | Mn | S (ppm) |
|---|---|---|---|---|
| 0.07 | 16.4 | 1.6 | 7.3 | 9 |

**Low Ni austenitic stainless steel**

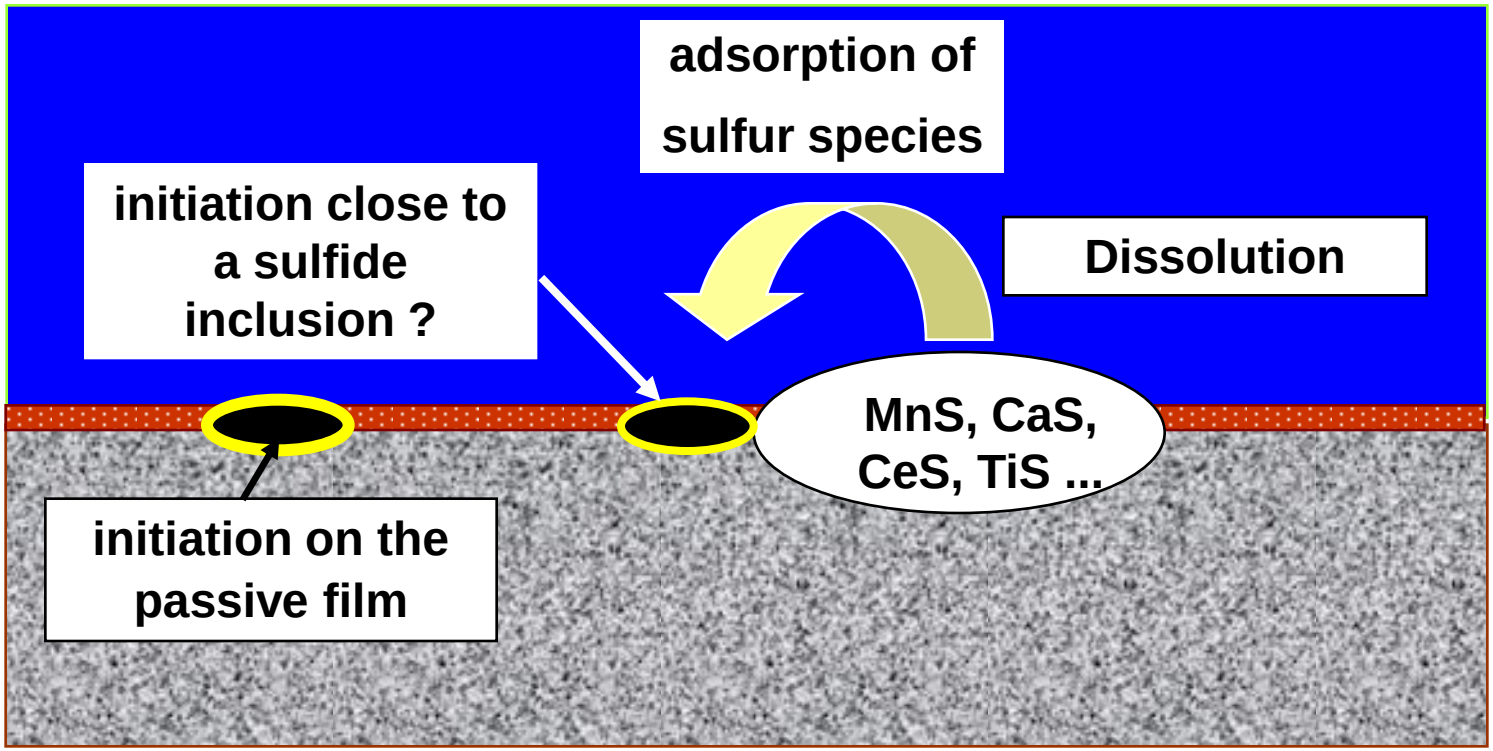
***The variations in pitting potential reveal***

***1) A significant effect of the sulfide solubility***

**+**

***2) An effect of the matrix composition (Ni in 304)***

# Modeling the effect of sulfides




•**The sulfides dissolve** **more or less rapidly , depending on their stability and on the solution corrosivity. In pitting initation the sulfides act simply as sulfur species provider**

•**Sulfur containing species** **adsorb on the passive film close to the sulfide inclusion,**

**Promoting pit nucleation**
(local film breakdown) or

**Preventing repassivation**
of nanopits

**The pitting potential** ***characterizes either***

**- the pit nucleation** ***or***

**- the stabilization of pit nuclei**

# Modeling the effect of sulfides (2)

- **The earlier theories**
  - **Sulfide dissolution, producing an unfilmed bare metal surface**
  - **Does not take into account the effect of passive film on pit initiation. Passive film could act only through the cathodic reaction (in OCP conditions)**

- **Effect of thiosulfates**
  - **Sulfide dissolution produce thiosulfates which prevent repassivation in the occluded zone formed by a metastable pit.**

- **The effect of sulfide solubility**
  - **Sulfide inclusions may act simply as sulfur species sources.**
  - **Sulfur containing species (elemental sulfur, thiosulfates…???) redeposit around the inclusion and make the passive film sensitive to pitting corrosion**
  - **Steel resistance to pitting decreases as sulfide inclusion solubility increases:**
    - **CaS < MnS < (Mn,Cr)S < CrS < TiS < CeS**

- **The Cr depletion theory** (Nature, Vol 415, 14 Feb. 2002) **does not meet basic metallurgical evidences**. More the effect of steel making process is ignored
  - In SS, Mn sulfides content a small amount of Cr (~5% in 304). The larger the Cr content or the smaller the Mn content, the larger the pitting resistance.
  - Ti containing steel, free from MnS but containing $Ti_xS$, resist better to pitting than MnS containing steels. They can pit however, but at higher potential , temperature or chloride content. Inclusions other than sulfides can also initiate pits
  - Metastable pitting was also observed even on « pure » (inclusion free) Fe17Cr alloys

# Conteracting the sulfur effects on pitting initation

*by T.Sourisseau and alias, Cors.Sci. 2005, 47, p1097*

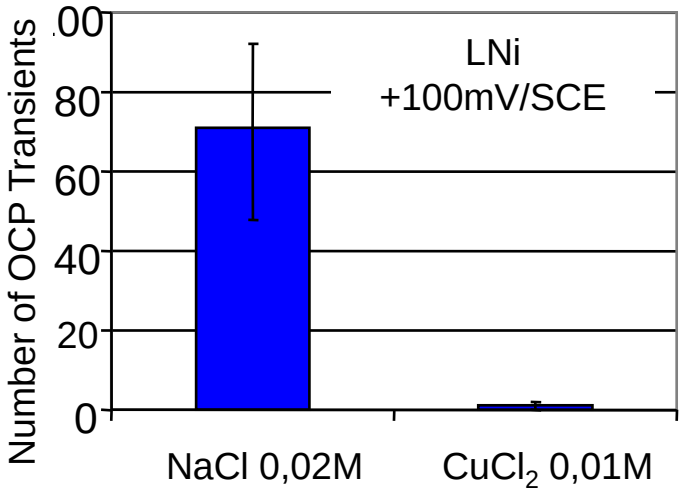
***When added in aqueous solution*,**

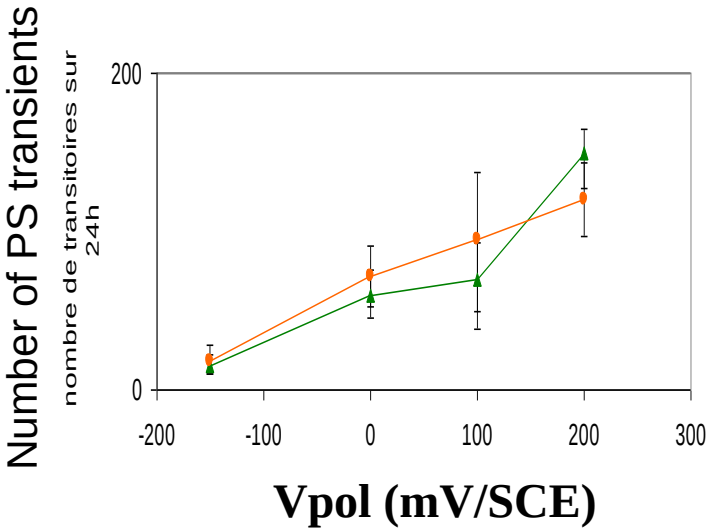
**Cu Inhibits pits initiation**

*(formation of insoluble CuS-Cu2S)*

***When added as alloying element***

**No effect is found on the number of transients**



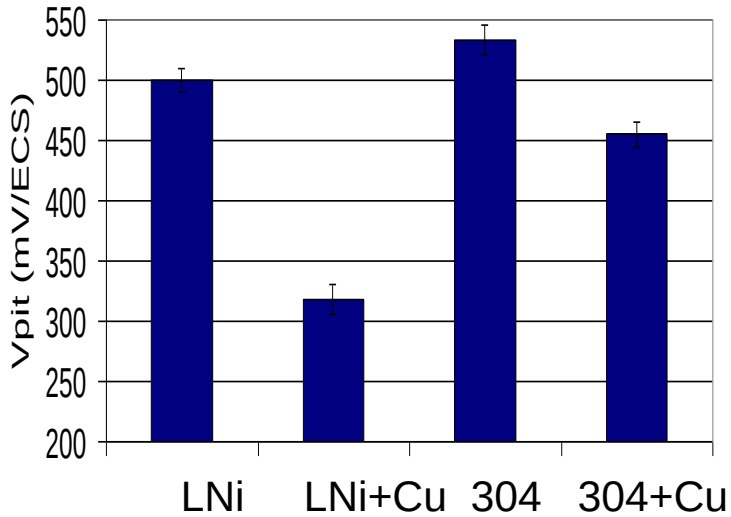

**The favourable effect of *dissolved copper* in preventing pit initiation is revealed by the number of pitting transients**

The possible effect **of *alloyed copper*** in preventing pit initiation ***is not revealed*** by the number of transients

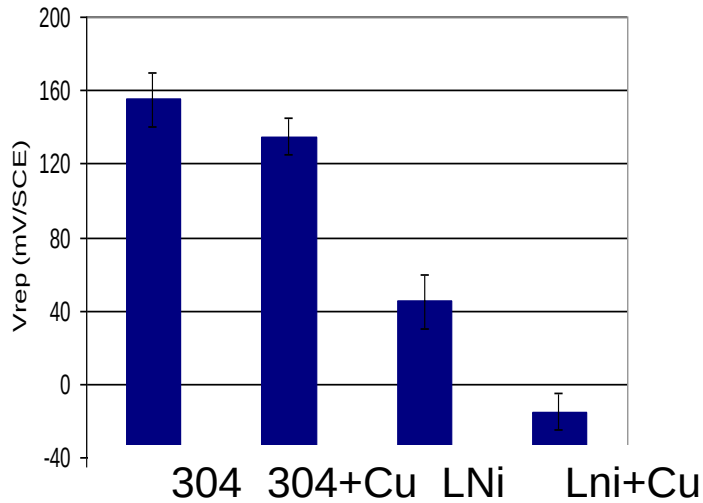
# Effect of metallic copper on the pitting potential

*by T.Sourisseau and alias, Cors.Sci 2005.*

Such an alloying addition of Cu is even found to decrease the pitting potential , and overmore the repassivation potential




**pitting potential**




**repassivation potential**

***1) Metalic Copper <u>hinders repassivation</u>***

*It was suggested that metallic Copper redeposits at pit bottom , inhibiting further Chromium oxidation, then preventing pit repassivation. The lower the pitting potential, the smaller the amount of dissolved Cu ions and then the larger the detrimental influence of Cu on the final result.*

*2) From the material performance viewpoint, it is worthy to note that this detrimental effect of Cu is revealed by both* ***repassivation <u>and pitting potential</u>***

# The effect of cold rolling

*by L..Peguet and alias, Cor.sci. In press)*

**Chemical composition of the investigated material in weight %.**

| Grade | Elaboration | % C | % Mn | % Ni | % Cr | % Mo | % Cu | S (ppm) | % N |
|---|---|---|---|---|---|---|---|---|---|
| **AISI 304** | *Laboratory* | 0.026 | 1.45 | 8.57 | 17.86 | 0.20 | 0.20 | 51 | 0.036 |

INGOTS
(25Kg)

*Forging (1250°C)*

PLATES
(section : 16mm×120mm)

*Hot rolling (1250°C)*

HOT ROLLED PLATES
(thickness: 1.5mm)

*Thermal treatment in salt bath (1100°C)*
*Pickling in acid bath ($HNO_3$, HF)*

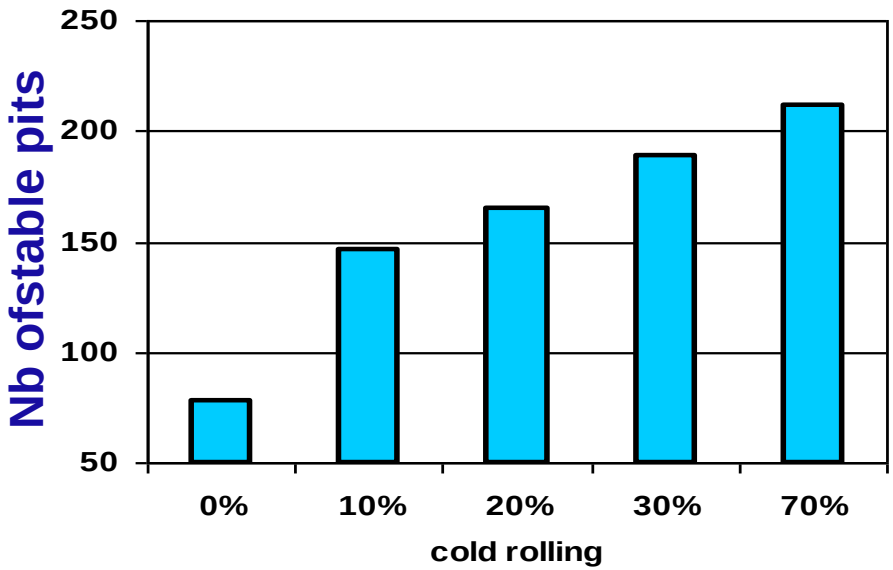
ANNEALED PLATES
(thickness: 1.5mm)

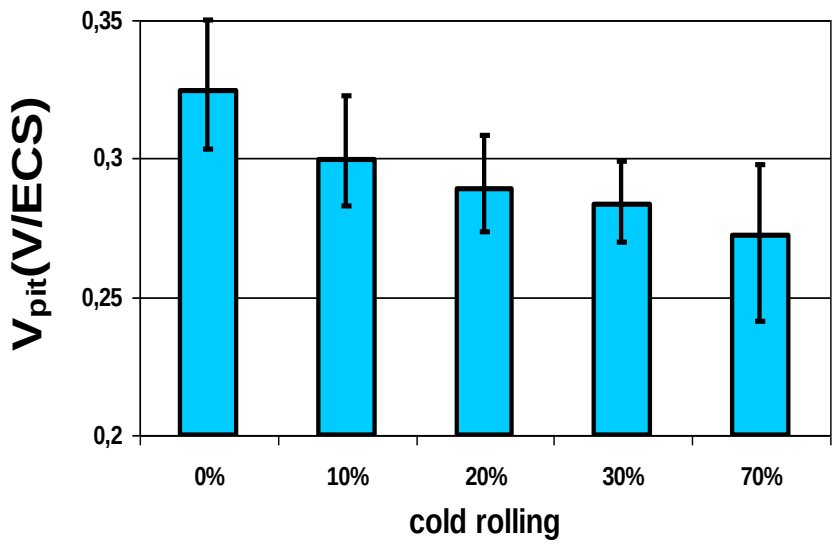
*Cold rolling (multi-pass)*

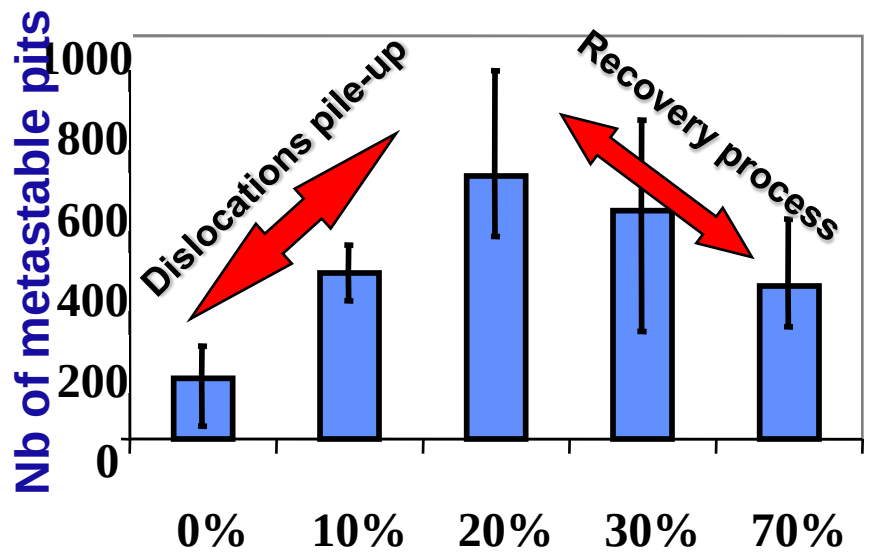
**COLD ROLLED PLATES**
**(reduction : 10, 20, 30, 70%)**

# The effect of cold rolling: results

A fair correlation is evidenced between the ***pitting potential*** and ***Stable pitting*** but ***not*** with the number of ***metastable pitting transients***




***In this case, the pitting potential is then correlated to stable pitting but not to the pit initiation sensitivity***

# Tensile deformation of a ferritic grade

*(no deformation martensite)*

Chemical composition of the investigated materials in weight %.

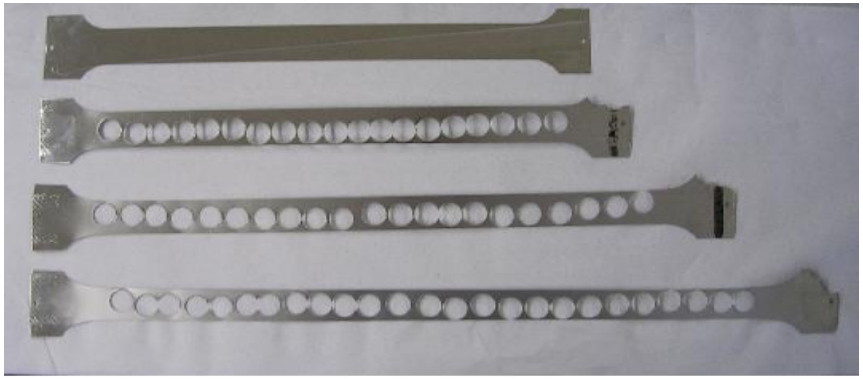
| Grade | Elaboration | % C | % Mn | % Ni | % Cr | % Mo | % Cu | S (ppm) | % N |
|---|---|---|---|---|---|---|---|---|---|
| AISI 304 | *Industrial* | 0.037 | 1.42 | 8.66 | 18.18 | 0.25 | 0.22 | 12 | 0.038 |
| AISI 430 | *Industrial* | 0.042 | 0.38 | 0.16 | 16.26 | 0.03 | 0.04 | 21 | 0.027 |

Annealed

10%

35%

60%



⇨ Disks stamped from strained samples to be used in electrochemical characterization.

Number of metastable pits initiated during 24h at free potential in NaCl 1M + $FeCl_3$ $10^{-3}$ M.

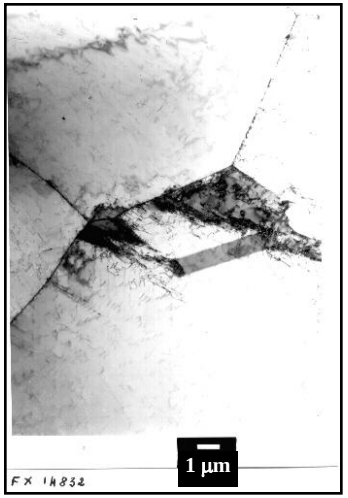
| | annealed | 10% | 20% | 35% | 60% |
|---|---|---|---|---|---|
| **AISI 304** | 116 | **297** | - | 64 | 40 |
| **AISI 430** | 371 | **515** | 309 | - | - |

⇨ **Even a ferritic grade exhibits a maximum in pit initiation.**

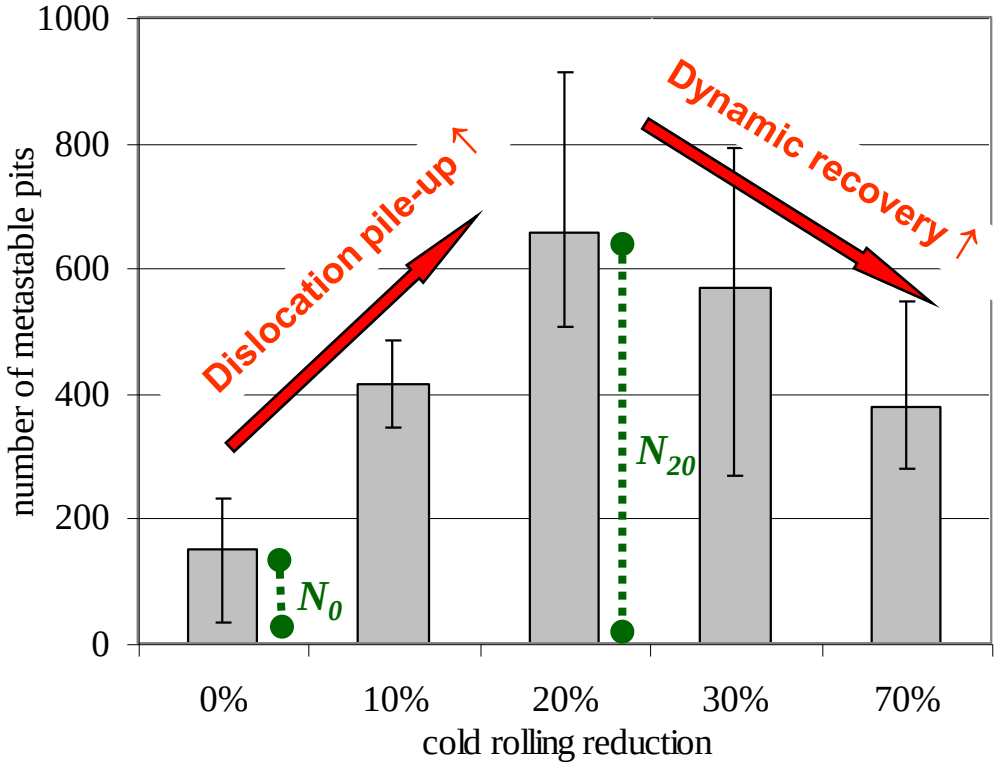
# Dislocations substructure


**20% colled-rolled**

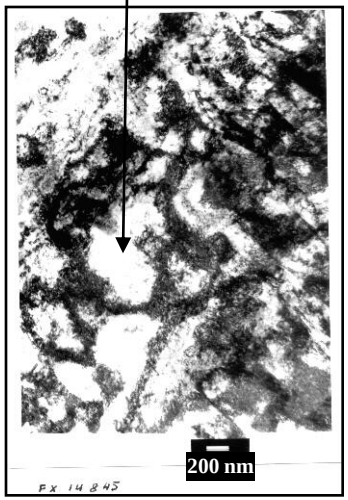
**Moderate strain : Fine lamellar structure by twinning, shear bands favoring dislocation pile-ups**




**Annealed**




**dislocations cells**

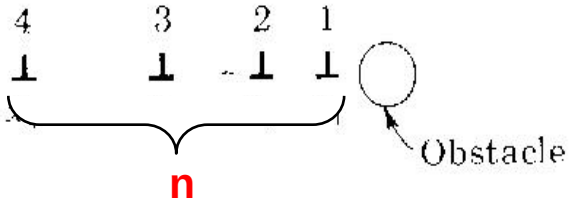



**70% colled rolled**

**Large strain : Recovery process illustrated by dislocations cells and pile-ups destruction.**

# Mechano-electrochemical modeling

## Dislocation Pile-ups

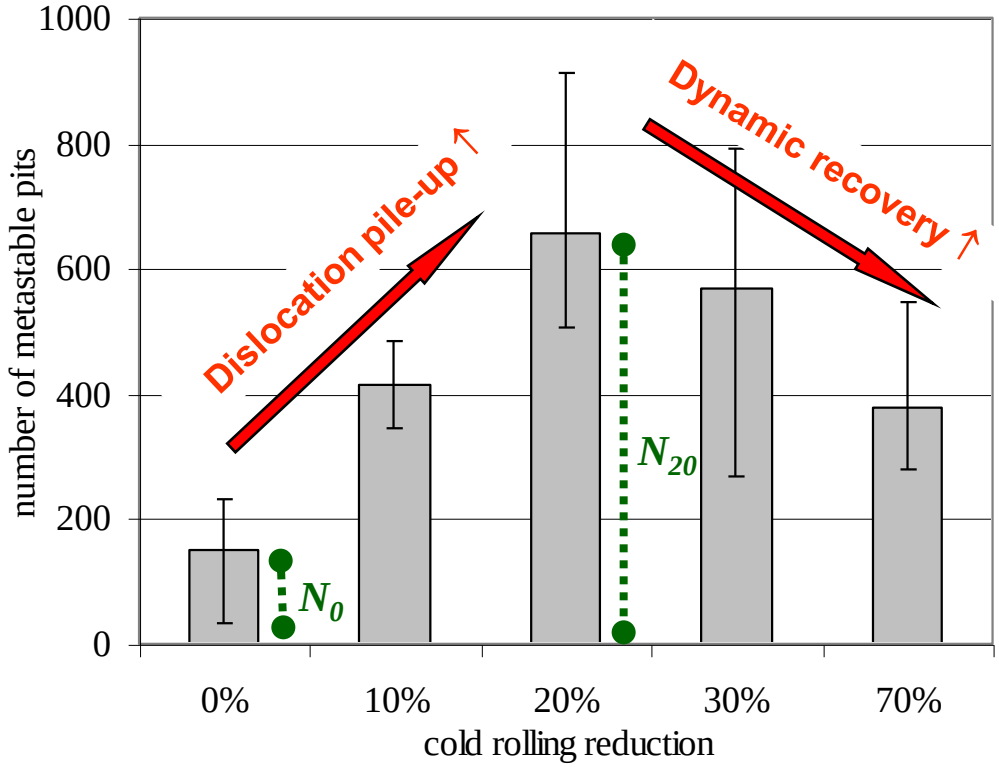



⇨ inducing large stress concentration:

$$\sigma \propto n$$

⇨ causing local electrochemical heterogeneities:

$$\Delta\varphi = -n\Delta\tau \frac{R}{\alpha R' zF}$$




**S.F.E. ↓ ⇒ Dislocation Pile-ups ↑**

- dissociation ↑
- cross slip ↓

⇩

**To work on selected SS grades with various S.F.E.**

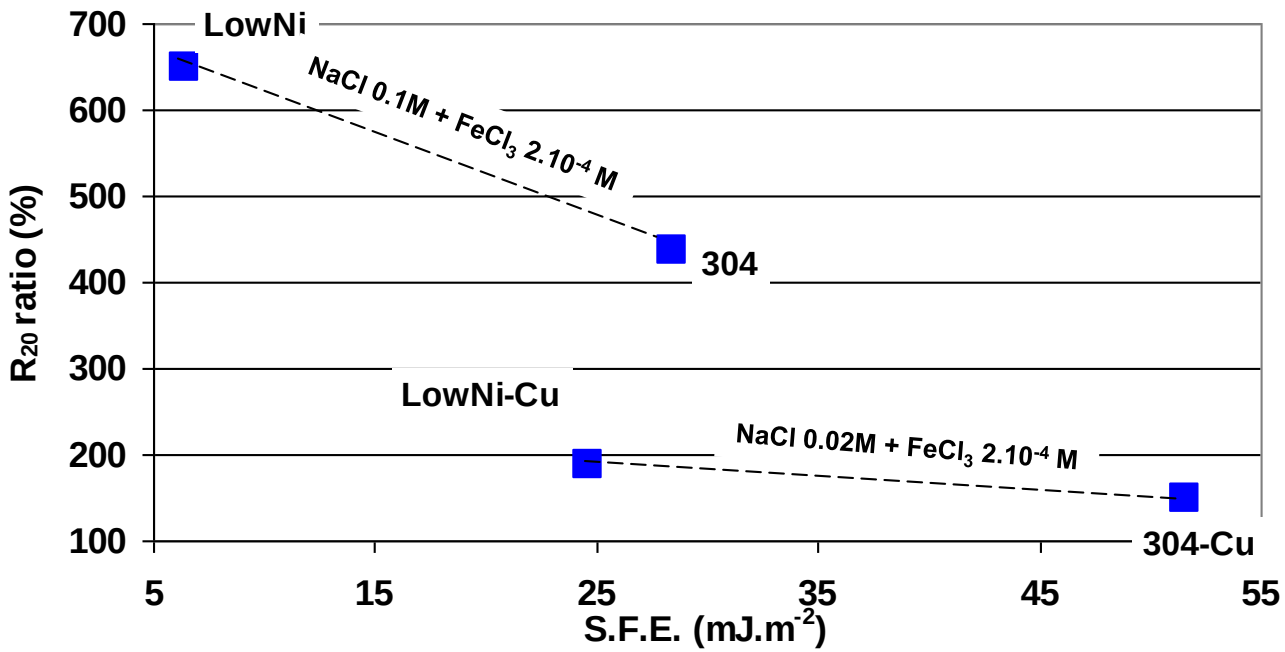
$$R_{20} = \frac{N_{20}}{N_0} = \frac{\text{Number of metastable pits at 20\%}}{\text{Number of metastable pits in the annealed state}}$$

# Alloying elements affect the extent of pit initiation frequency maximum via their influence on dislocation pile-ups stability.

| | C | N | S (ppm) | Cr | Mn | Ni | Cu |
|---|---|---|---|---|---|---|---|
| 304 | **0.03** | **0.04** | **51** | **17.9** | **1.5** | **8.5** | **0.2** |
| LowNi | **0.07** | 0.24 | **9** | **16.4** | 7.3 | 1.6 | **0.2** |
| 304-Cu | **0.04** | **0.04** | **45** | **18.2** | **1.4** | **8.7** | 3.0 |
| LowNi-Cu | **0.06** | 0.19 | **20** | **16.5** | 7.7 | 1.8 | 2.9 |

**SFE (mJ.m-2) = 25.7+2(%Ni)+410(%C)-0.9(%Cr)-77(%N)-13(%Si)-1.2(%Mn)+4(%Cu)**

Pickering (1984) - Dulieu, Nutting (1964)

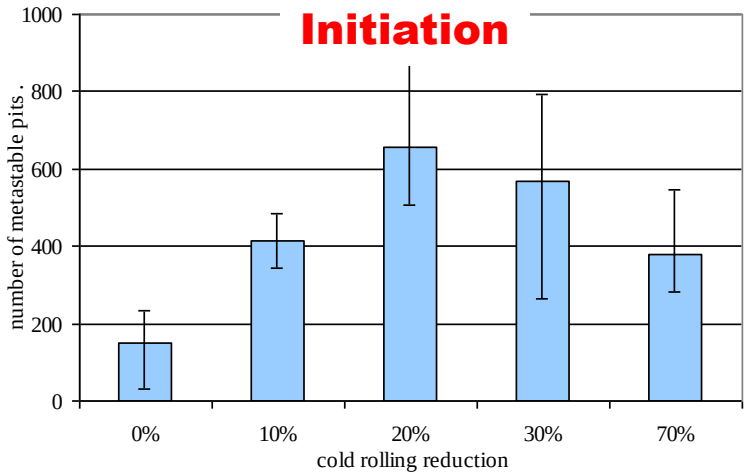


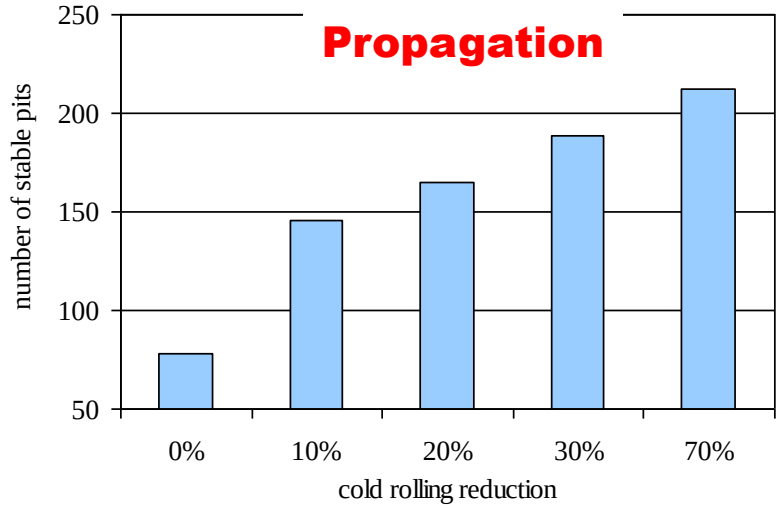

**S.F.E. ↓ ⇒ Pile-up ↑**

**⇒ $R_{20}$ ↑**

# The effect of cold rolling: Conclusions

⇨ **Plastic deformation acts differently depending on the pitting stage under consideration.**




⇨ **The unexpected maximum in pit initiation frequency does not depend on the deformation process nor on the presence of induced-martensite.**

⇨ **A major influence of dislocation pile-ups via the mecano-electrochemical effect is suspected. This explanation is supported by the role of alloying elements in the extent of pit initiation frequency maximum.**

# Effect of the surface finish condition on metastable pitting

*by G.Berthomé and alias, Cors Sci.*

The last stage of steel making process after cold rolling is the final annealing.

Two main conditions are of industrial interest for S.S. sheets:

**2B condition:**

**Cold rolled sheet + annealing in oxidizing atmosphere**

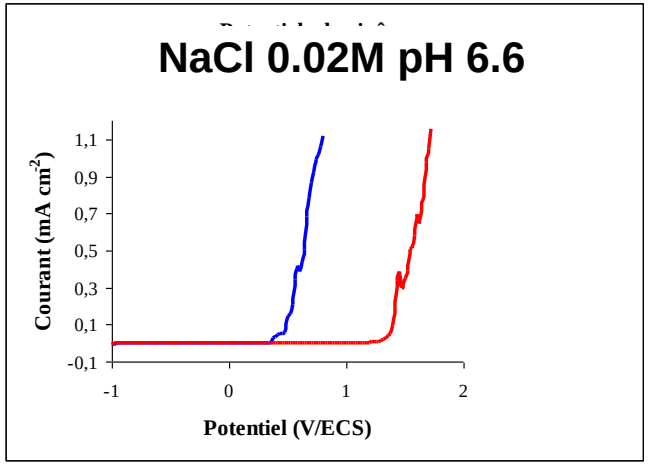
**+ pickling in acidic bath then rinsing + skin pass**

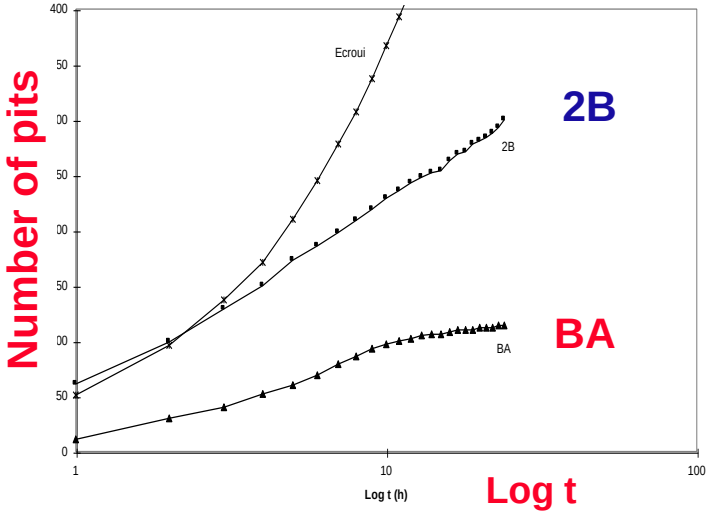
**BA condition:**

**Cold rolled sheet + annealing in H2 containing atmosphere + skin pass**

This produces some passive films of different Cr content and of different pitting corrosion resistances

The pitting potential is larger for BA than for 2B and the number of OCP pitting transients is smaller



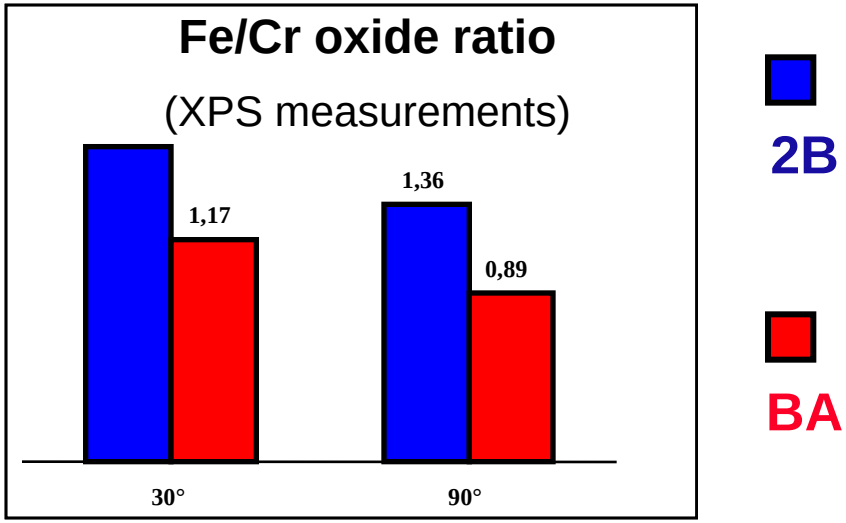

**Pitting potential:BA > 2B**

Number of pitting transients:

As rolled > 2B > BA

# XPS analysis

**The passive films fromed on 2B and BA differ by their chromium content and their semi conductive properties**

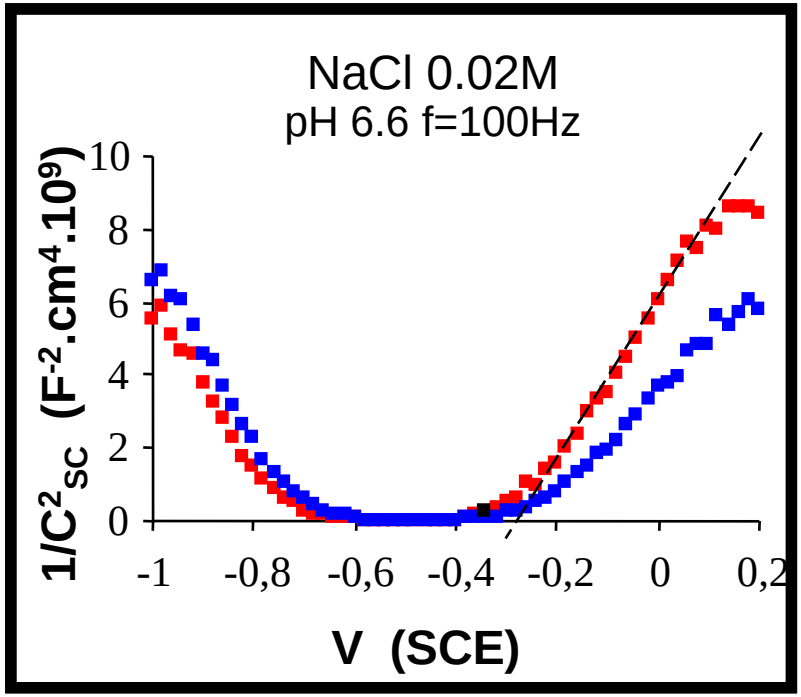



**In the two cases the Cr content is higher in the inner passive film than in the outer, and larger for BA than for 2B condition**

# Semiconductive behaviour

*byJ.Amri and alias: in preparation*

**The passive film exhibits a p-type inner part and a n-type outer part. The electron states densities (acceptors in the inner part, donnors in the outer part) are given by the Mott Schottky plots**




$$\frac{1}{C_{sc}^{2}} = \left| \frac{2}{\varepsilon_r . \varepsilon_0 . q . N_q} (V - V_{fb}) \right|$$

**Mott-Schottky plots**

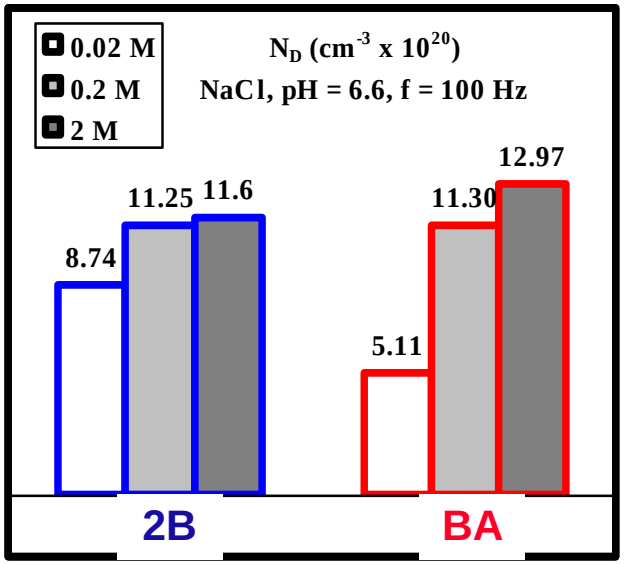
**2B : $N_d = 8.74 \,.\, 10^{20}$ cm$^3$**

**BA : $N_d = 5.11 \,.\, 10^{20}$ cm$^3$**

**Thhe electron donnor concentration in the outer passive film (which is likely related to the concentration in point defects) is smaller for BA than for 2B,**

# Going further (2)

*byJ.Amri and alias: in preparation*




**The density of donnor states increases with the electrolyte chloride content,**

**Suggesting that the corresponding point defects are due to Chloride ions adsorption or incorporation in the outer passive film**

**Following this idea, the 2B film is less corrosion resistant due to its larger affinity for chloride ions**

**In this case the rate determining step is likely the nucleation step, and**

**the pitting potential and the number of transients are fairly correlated to the Pit nucleation sensitivity**

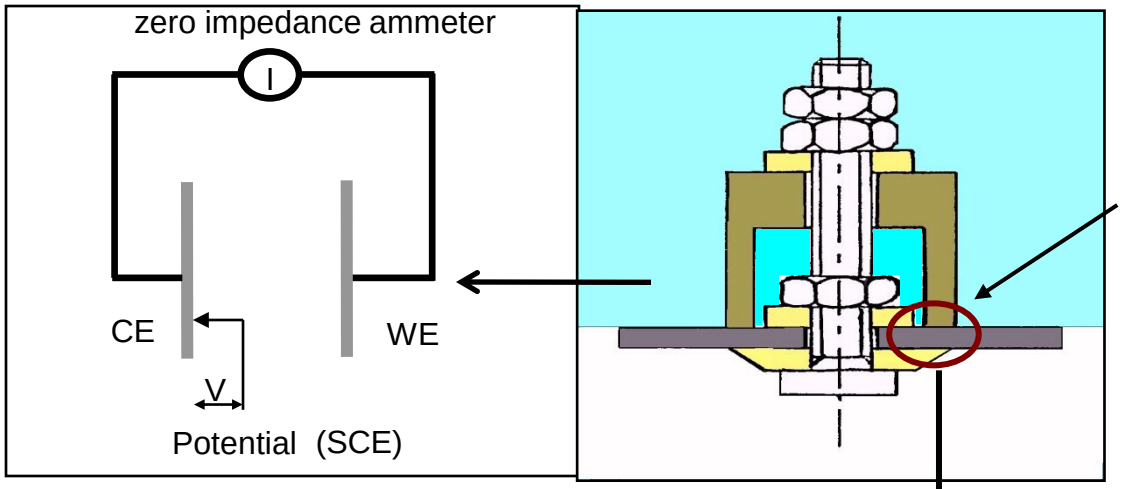
# Effect of the Surface Condition on the resistance to CC

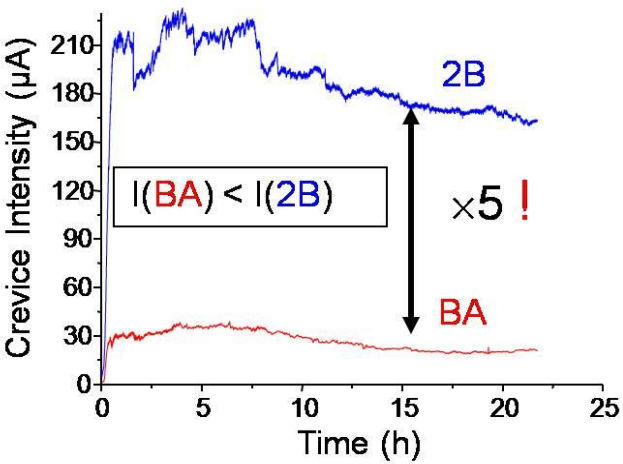
**Material:** Fe17Cr

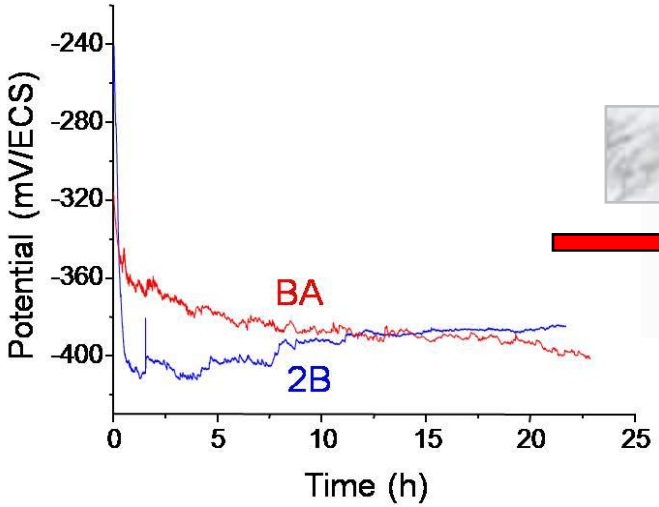
**Surface finishing** :

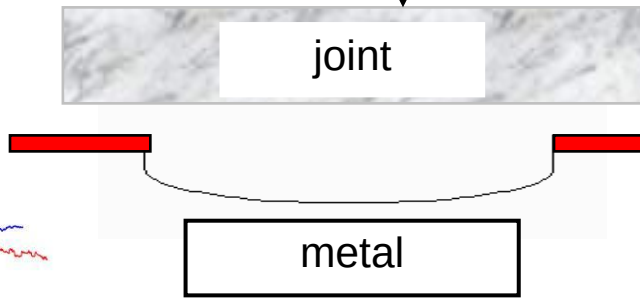
BA *(Bright annealed)*
2B *(Pickled surface)*

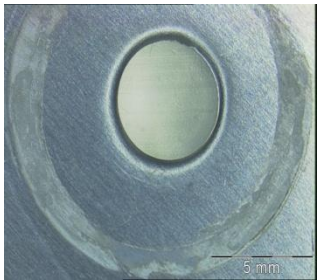
**Test conditions:**
NaCl 0.5M pH 6.6 / 50°C
Screw/wing system
tightening = 0,2 N.m
$S_{crev}$ = 0.85 cm$^2$



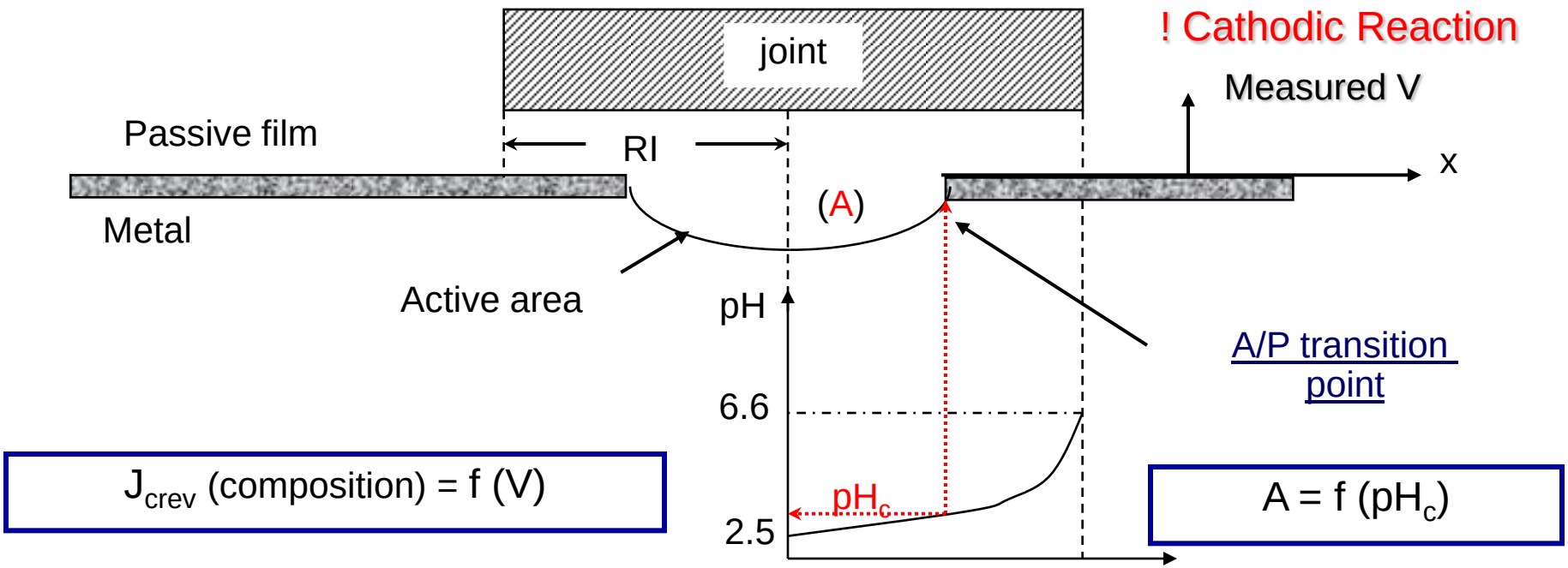




The active area 2B is ~ 5 times larger for 2B than for BA

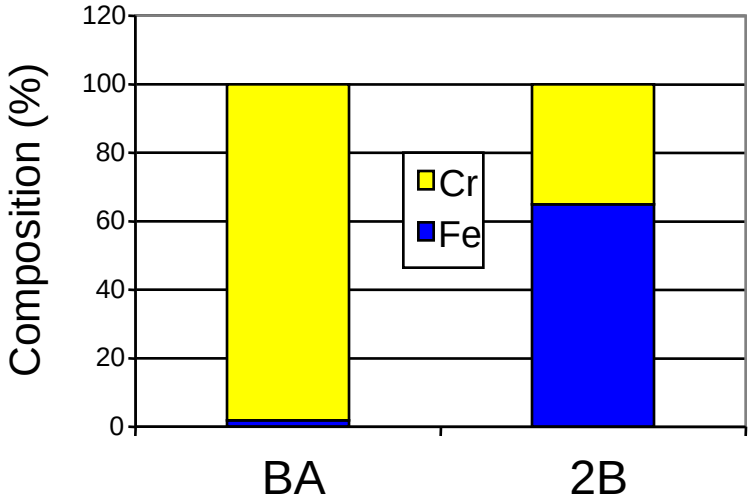
**Then $j_{crev}$(2B) = $j_{crev}$(2B)**

# Effect of the Surface Condition (2)




✓BA finish exhibits better crevice corrosion resistance then 2B.

✓ The corrosion current is controlled by the the active area, depending on the critical depassivation pH



# Corrosion feuilletante des allaiges d'aluminium

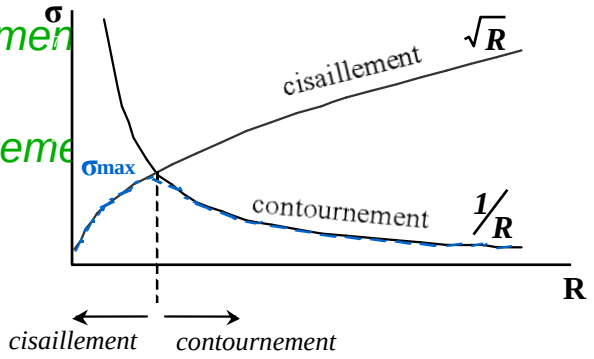
Alliages 7000 (aéronautique) à durcissement structural : précipitation durcissante type $MgZn_2$

Franchissement des obstacles (précipités) par les dislocations:

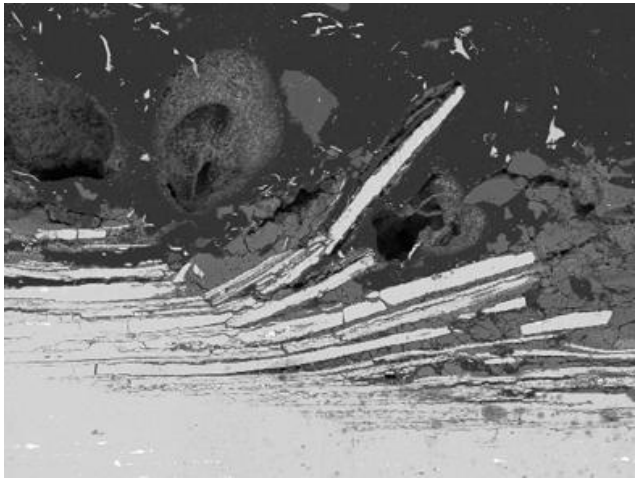
$$\Delta\tau = K.f_v^{1/2}.r^{1/2} \text{ - Cisaillement}$$

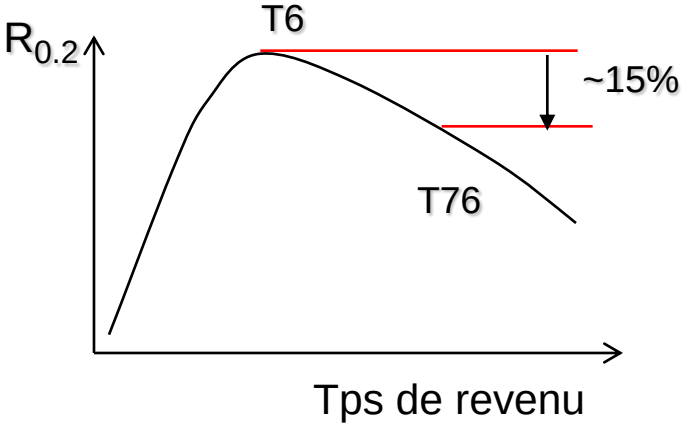
$$\Delta\tau = K.f_v^{1/2}.\frac{1}{r} \text{ - Contournement}$$

⇒Taille optimale de précipités




. Excellentes propriétés mécaniques ($R_{0.2}$ : 430-700 Mpa ) MAIS sensibilité à la corrosion feuilletante





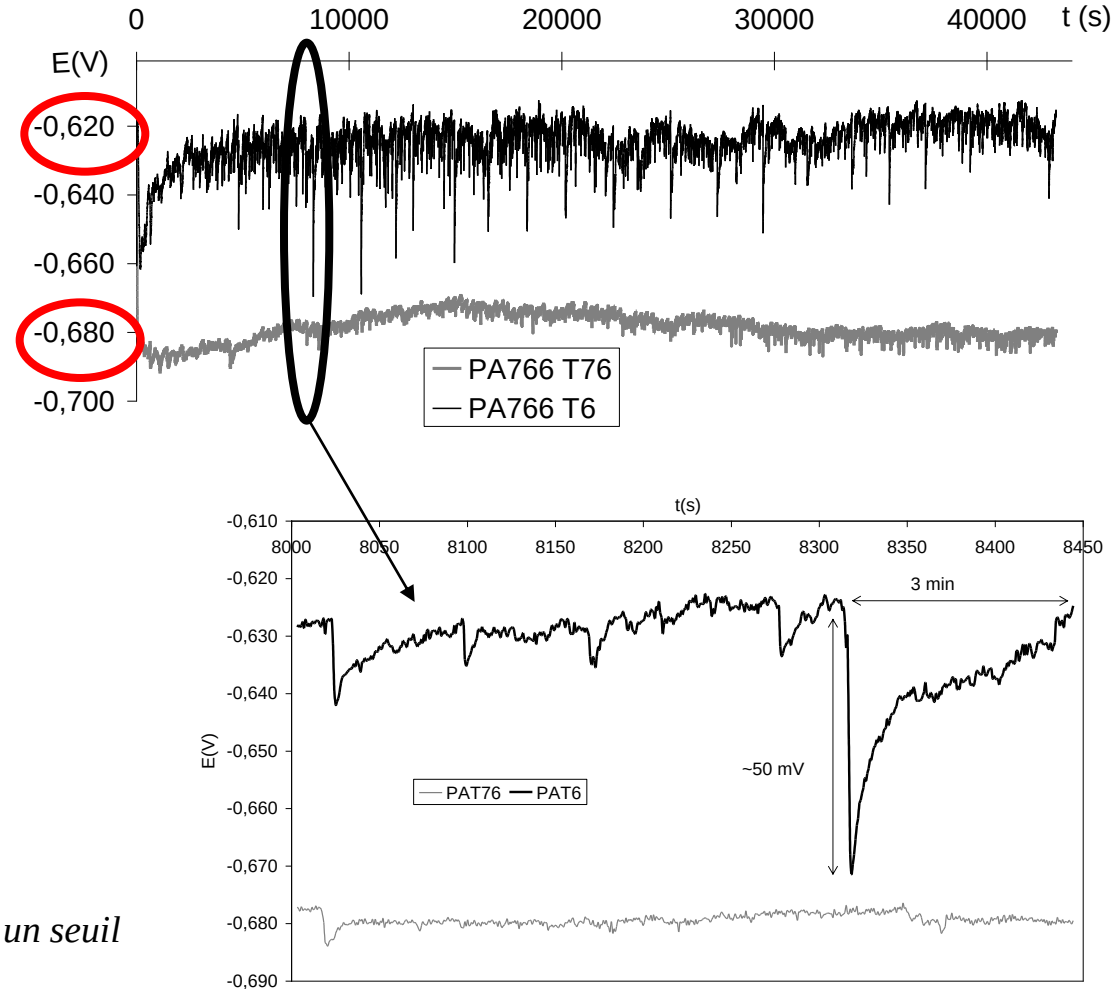

- <u>T6</u> : Revenu au pic = maximum de caractéristiques mécaniques
- <u>T76</u> : Sur-revenu = compromis entre CM et sensibilité à la corrosion feuilletante

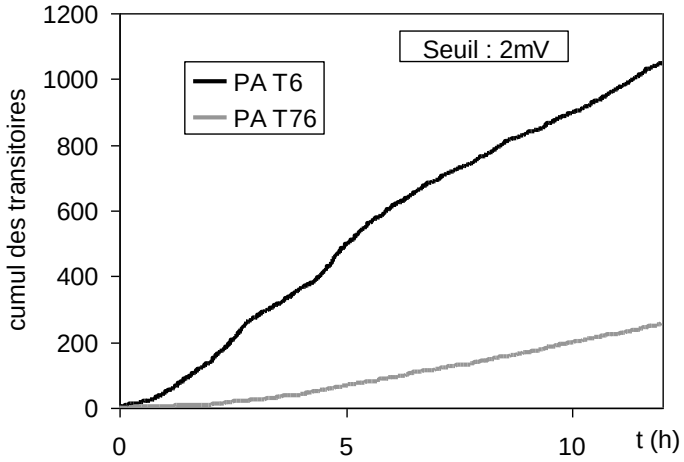
# Essai galvanostatique

**Solution** :
NaCl 1M, $NaNO_3$ 0.25M, $AlCl_3$ 0.033M
**Intensité** : 2.5mA/cm$^2$
**Aspect**: T6 = feuillets, T76 = poudre

Les transitoires en potentiel =

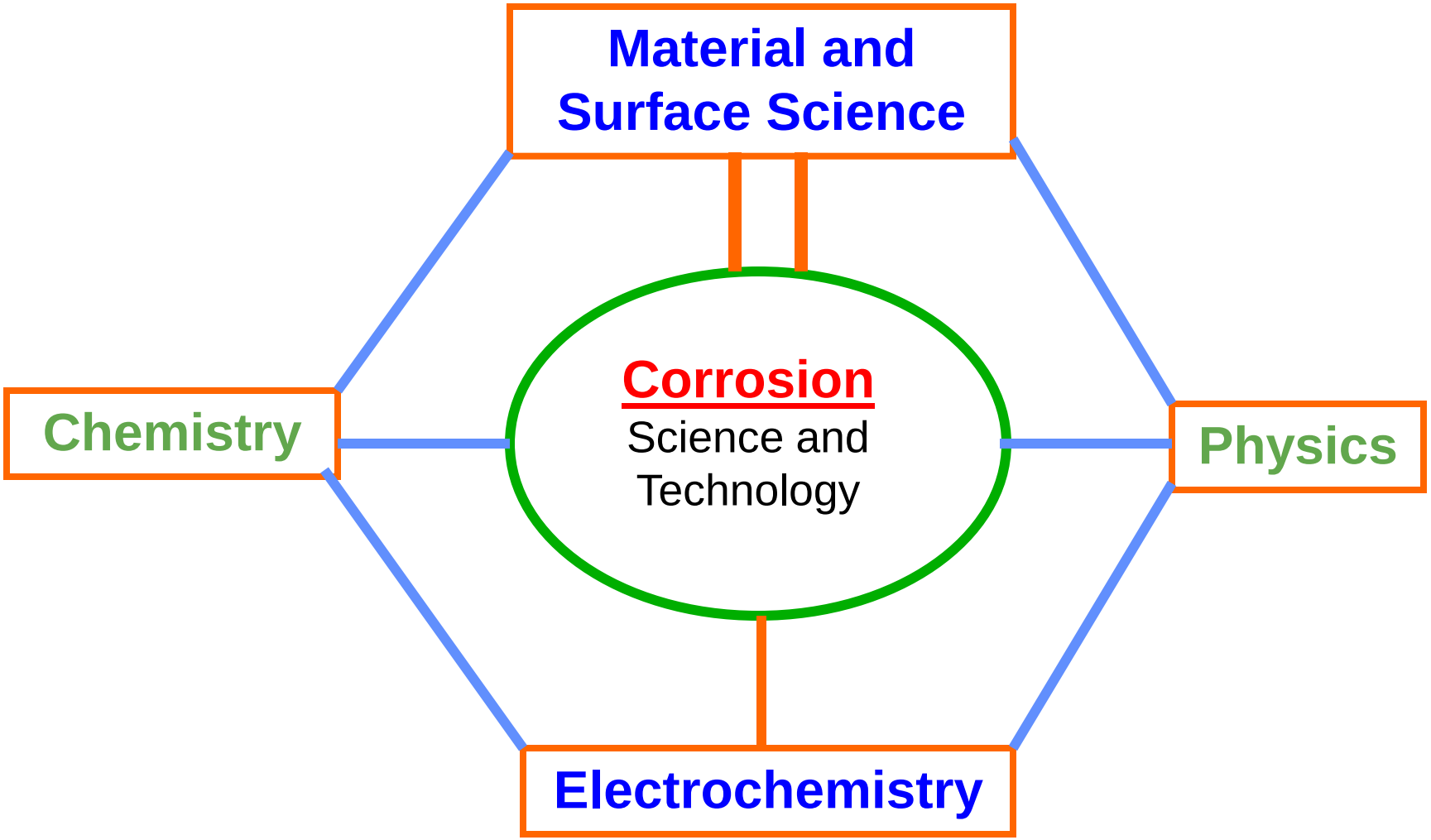
Corrosion feuilletante



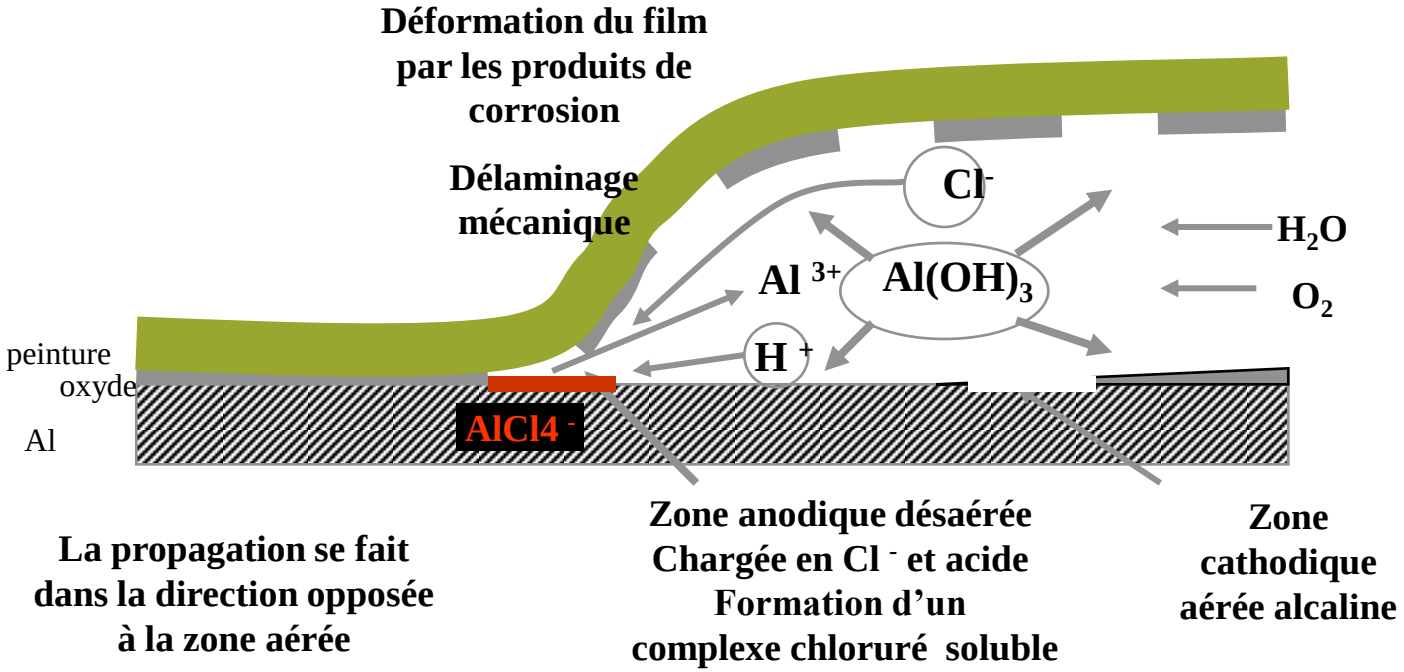

*Cumul du nombre de transitoires supérieurs à un seuil de 2mV à droite*

# Conclusion:
# The importance of being a metallurgist



# Délamination des peintures

## Délamination anodique




## Délamination cathodique *(Propagation à l 'interface peinture/oxyde)*