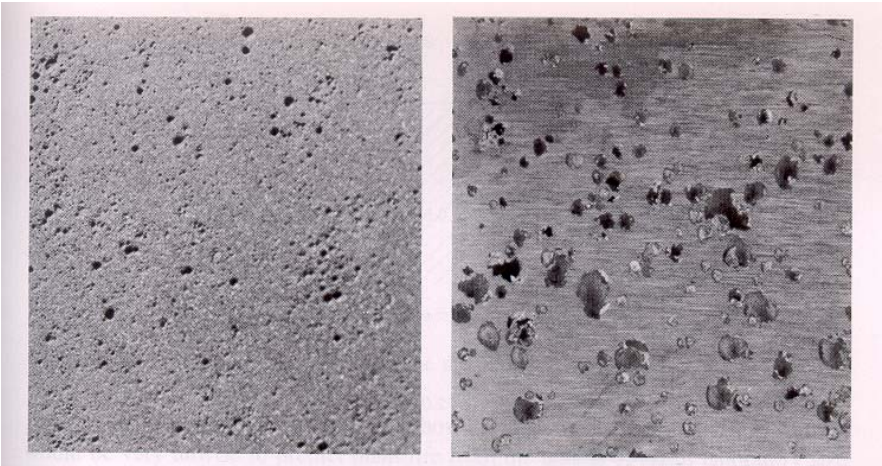
12. Pitting Corrosion

A form of extremely localized attack that results in holes in the metal.
occurs in passive alloys ; pitting corrosion requires a passive external surface that can provide a high potential to cause the current to flow into the pit; if the external surface is active, this driving force is not available

- Initiated by localized breakdown of passive film, usually by Cl^-.
- Difficult to detect pits because of their small size.
- Pitting requires an extended initiation period before visible pits appear. Once started, a pit penetrates the metal at an increasing rate.
- Growth mechanism of pit is identical to that of crevices. The cause of the initiation of pitting corrosion is still not clarified.



12.1 Process of pitting corrosion

Film breakdown

↓

Metastable pitting :

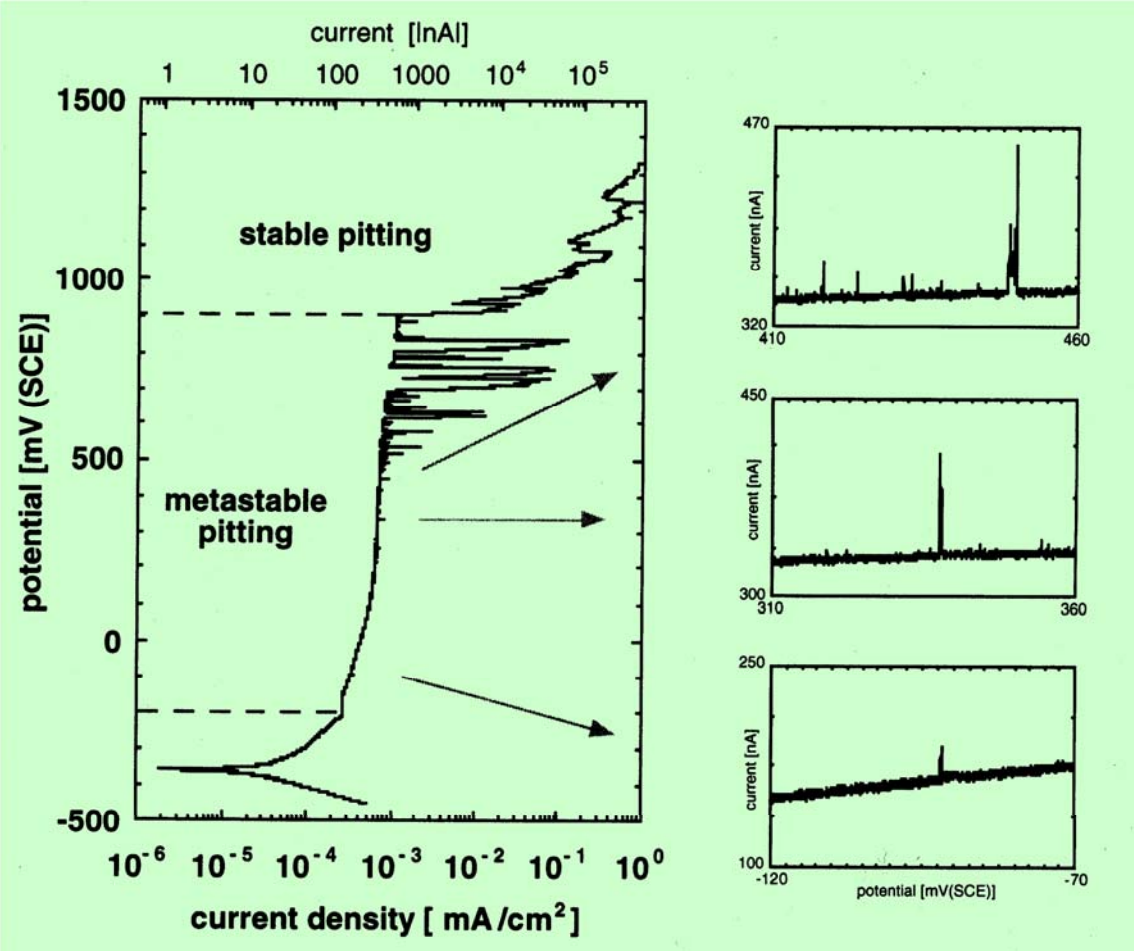
Pit initiation ⇔ Repassivation

↓

Stable pitting : Pit Growth

↓↑

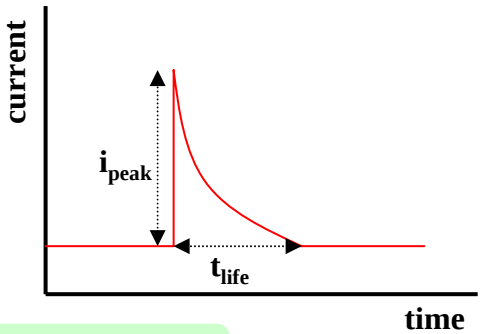
Death with repassivation



Typical potential current curve of stainless steel in Cl^- showing the different stages of localized corrosion.

1. Film breakdown : Film breakdown is a precursor for pitting corrosion, and occurs by chemical attack of Cl^- or by mechanical means. Film breakdown for stable growth of pitting occurs at potentials above E_{pit} that is indicated by the abrupt increase in the anodic polarization curve.

2. Metastable pitting :Pits that initiate and grow for a limited period before repassivation. At stage of metastable pitting that occurs at potentials lower than E_{pit}, pit initiation is followed by rapid repassivation. The resulting current transients differ widely with respect to the i_{peak} as well as the life time (t_{life}). :

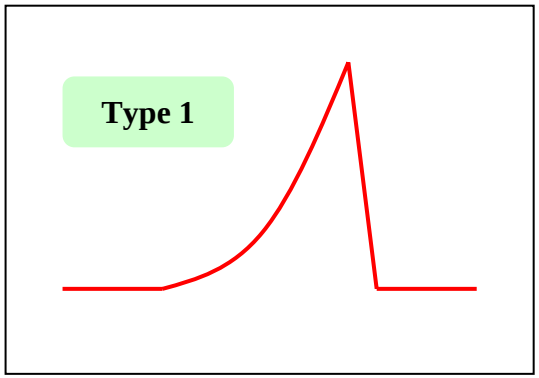


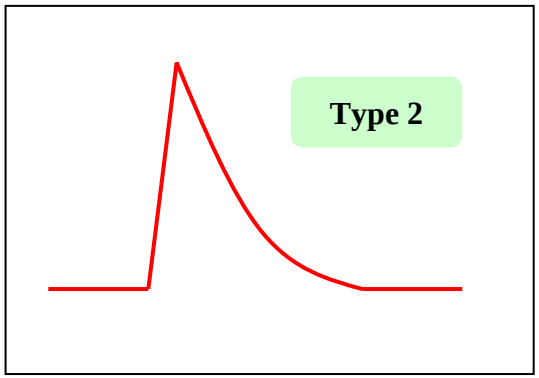
↑ E_{app} : leads to larger current transients with higher i_{peak} and longer t_{life}.

- At $E_{app}>E_{pit}$, or potential range, a transition from metastable pit to stable pit occurs. Even above E_{pit}, repassivation may still occur, showing the stochastic character of localized corrosion processes.
- The occurrence of metastable pitting below the E_{pit} indicates a potential risk, especially when crevice conditions cannot be completely excluded.
- The metastable pitting behavior of an alloy is evaluated by counting the event density of metastable pits (# of peaks/area) or plotting the power spectrum density as a function of frequency.

▶ *Types of current transients of metastable pitting*

	Type 1	Type 2
Appearance	Slow growth Rapid repassivation	Rapid growth Slow repassivation
Material	MnS-containing steel	MnS-free steel
Peak height	0.1 to 1μA	10 to 100 nA
Pit morphology	Occluded	Opened





▶ *Analysis method : Power Spectrum Density (PSD)*

PSD : Electrochemical noise analysis **in frequency domain**

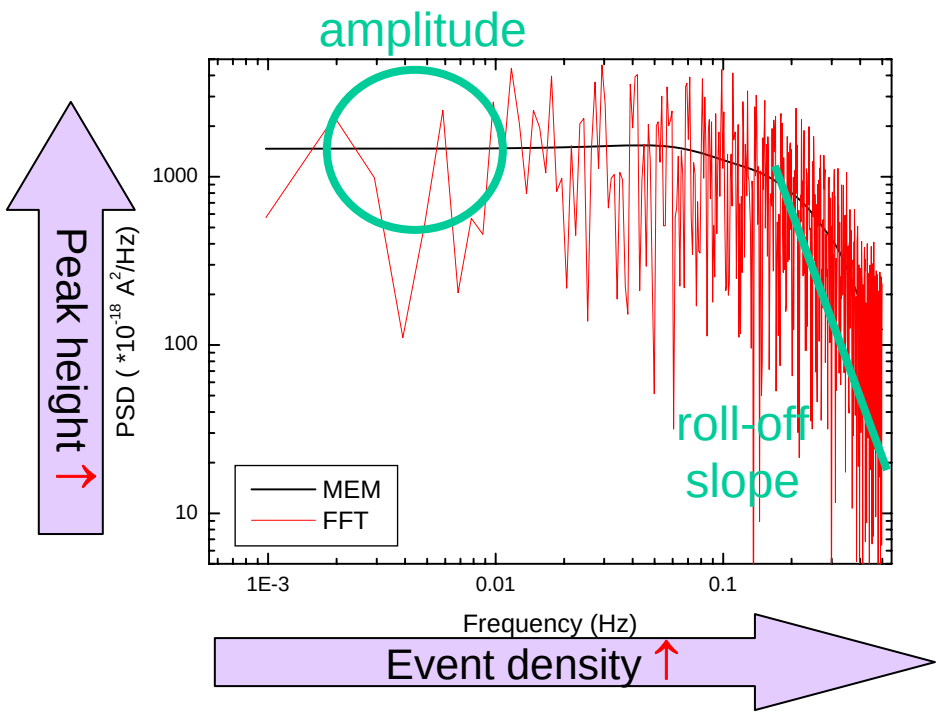
PSD

$$\Psi(f) = \frac{2}{T}\frac{1}{K}\sum_{j=1}^{K}\left|I_j(f)\right|^2$$

f : frequency, $I_j(f)$: Fourier transform of the jth time record $I_j(t)$ of length T, K : the number of time record averaged

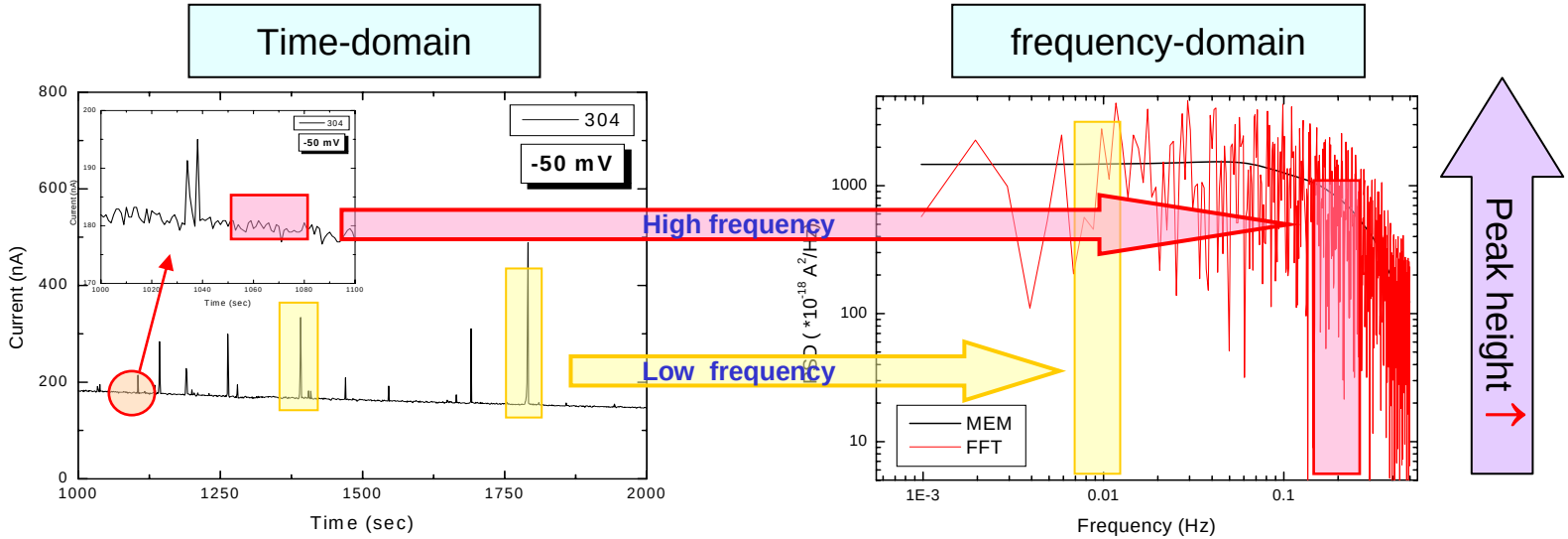
Methods

- FFT
  - Fast Fourier Transform
- MEM
  - Maximum Entropy Method



Important factor : *Amplitude in low frequency, roll-off slope*

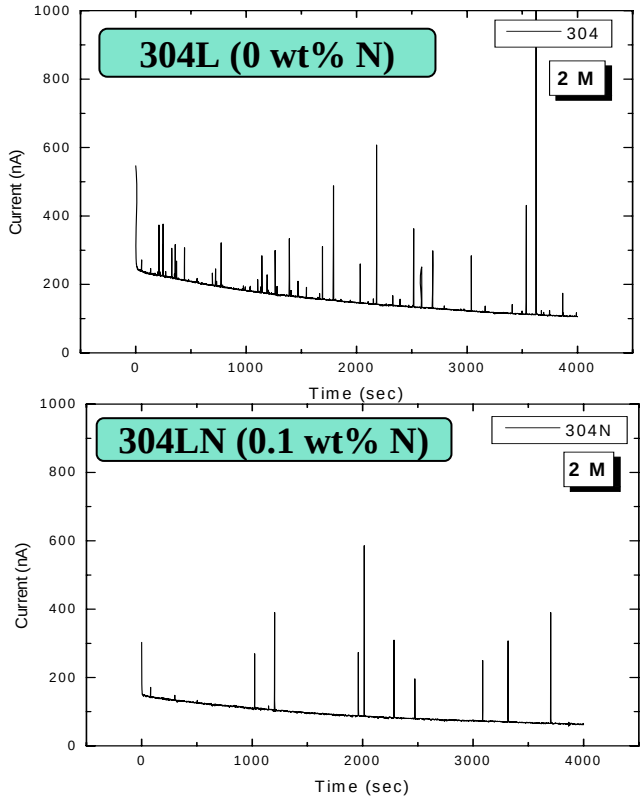
▶ *Amplitude in low frequency in PSD plot*

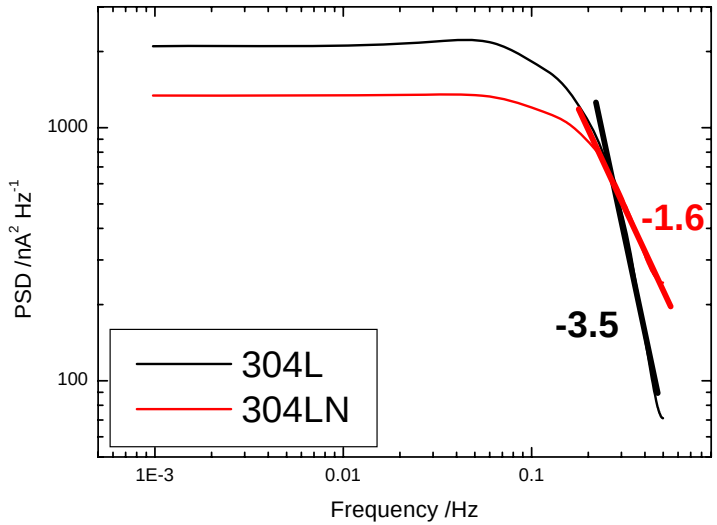


High amplitude in low frequency range means that current transients of metastable pitting have high intensity.

Amplitude in low frequency ↑ ⇨ **Pitting Susceptibility** ↑

▶ *ENA results of STS 304L and STS 304LN*



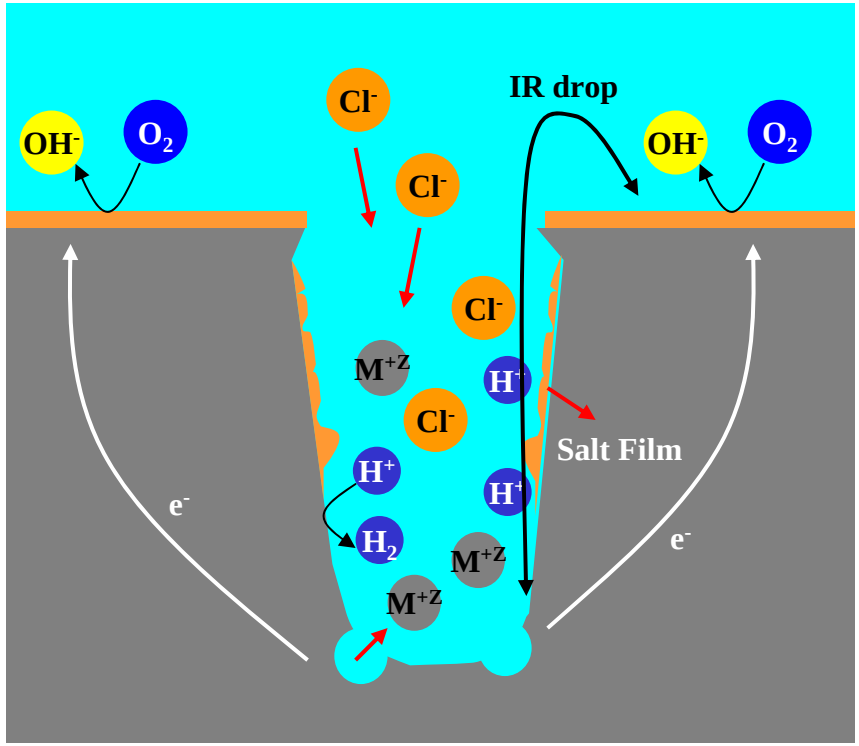


Nitrogen ↑ ⇨ *ED ↓, Amplitude ↓, roll-off slope ↓*

⇨ **Resistance to metastable pitting ↑**

12.2. Growth mechanism of pitting corrosion - Autocatalytic nature of pitting corrosion

- Pitting corrosion occurs by the breakdown of passive film. Cl^- is detrimental in breaking the passive film.
- Mixing electrolytes in the pit with bulk solution is highly restricted ; major concentration difference is built up; low pH and high $[Cl^-]$.
- Large cathode area(external surface) and small anode area(pit).
- External surface is generally passivated due to high O_2 + high pH or cathodically protected.
- Within a pit ;
  i) Rapid metal dissolution(anodic dissolution).
  ii) Increase in $[Cl^-]$
  iii) Hydrolysis reaction by cation leads to acidification of solution



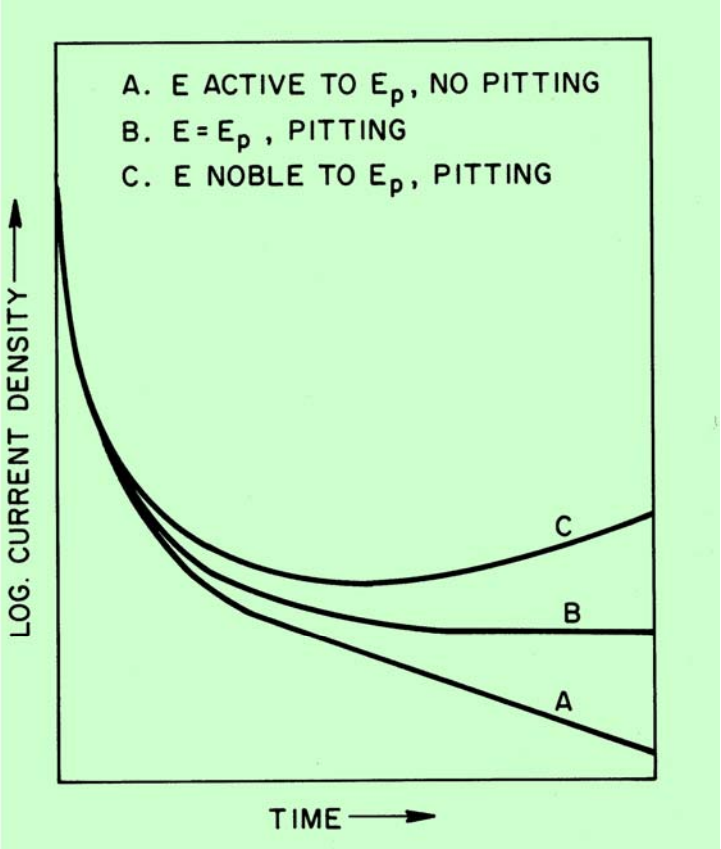
- In addition to O_2 reduction on the external surface, hydrogen reduction also takes place on the adjacent surface and hydrogen bubbles is formed at the pit wall, which increase the IR drop and often results in hydrogen embrittlement under loading.
- IR drop through the film and along electrolyte path between occluded region(pit) and external surface maintains potential difference (driving force) to keep actively corroding.
- Pitting corrosion is stopped when pit internal and external solutions are mixed; pits are repassivated.
- Once pits are formed, they propagate at an increasing rate in an autocatalytic nature.

12.3 How to evaluate the tendency of a metal to pitting corrosion

1) Film breakdown potential or pitting potential.
2) Critical pitting temperature.
3) Minimum [Cl^-] causing pitting.
4) Measurements of the number and the depth of pits in a suitable standard solution.

12.3.1 Pitting potential, E_{pit}

Pits are initiated by film breakdown of passive film due to an attack of halogen ions, especially Cl^- ion. These halogen ions have less effect on the anodic behavior of Ti, Ta, Mo, W, and Zr.



1) How to measure E_{pit}

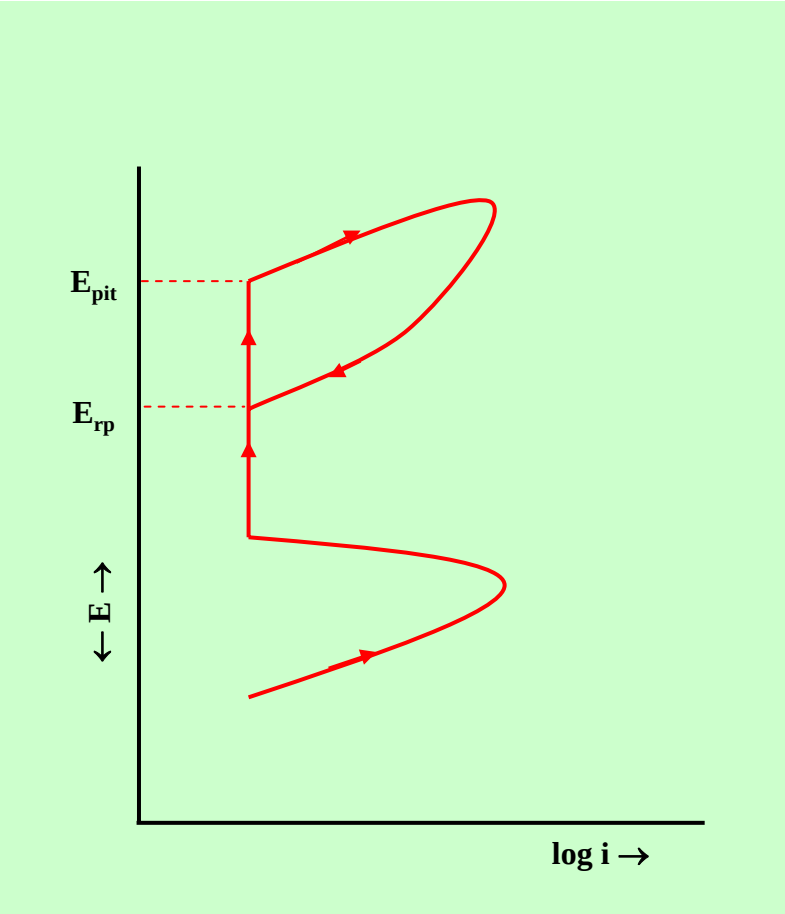
A. Potentiostatic method;

The E_{pit} is obtained by holding the specimen at various applied potentials near E_{pit}, and then plotting the current decay curve. When $E_{app} = E_{pit}$, the current decays to a constant value with time.

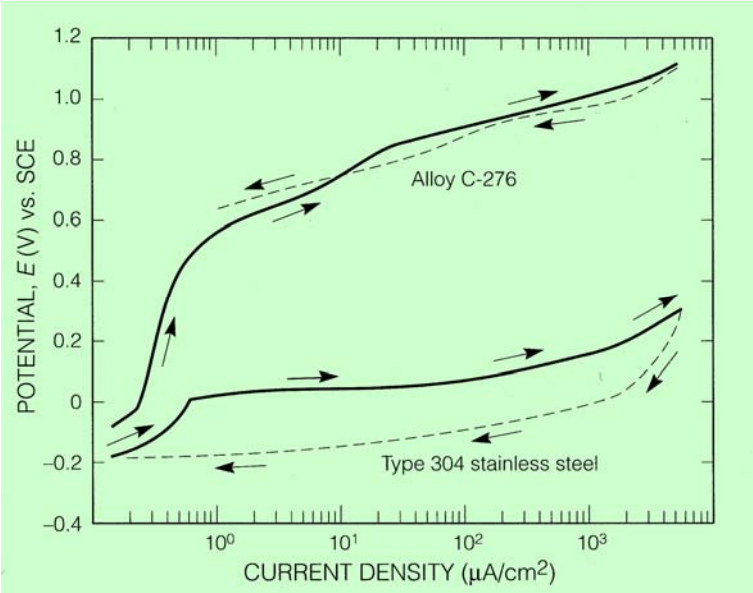
B. Potentiodynamic method;

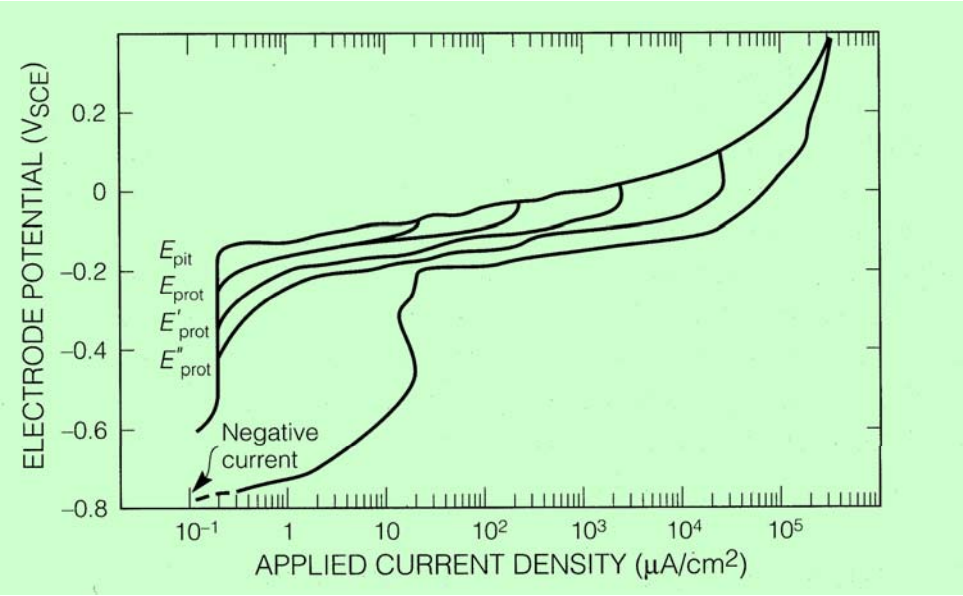
- Measure the current density with changing the potential gradually at a constant scanning rate and determine the critical potential (E_{pit}) at which the current density increases abruptly due to film breakdown.
- Protection potential for pits or a repassivation potential for pits is obtained when the measurements are done in reverse direction. If no pitting occurs, the curve traces the same path on reversing. On the other hand, if the alloy has undergone pitting, then we will get a hysteresis loop due to the film breakdown and pit formation.
- With reducing the potential, repassivation of pits starts and finishes until we reach the potential E_{rp} when the pits have been repassivated.

a. $E<E_{pit}$: Pits nucleation occurs.
b. $E_{rp}<E<E_{pit}$: New pits can not be formed, but the existing pits may propagate
c. $E<E_{rp}$: the metal remains passive.



- A metal in which E_{corr} is lower than E_{rp} would not undergo pitting corrosion.
- The area in the hysteresis loop under identical conditions(i.e, potential sweep reversal at the same applied current density) is directly related to the resistance of the alloy to the propagation of crevice corrosion.
- The difference in sweep rate can vary the value E_{pit}; Higher the sweep rate, the E_b increases.





12.4 Effect of electrolyte composition on the pitting

1) Effect of $[Cl^-]$ on E_{pit}

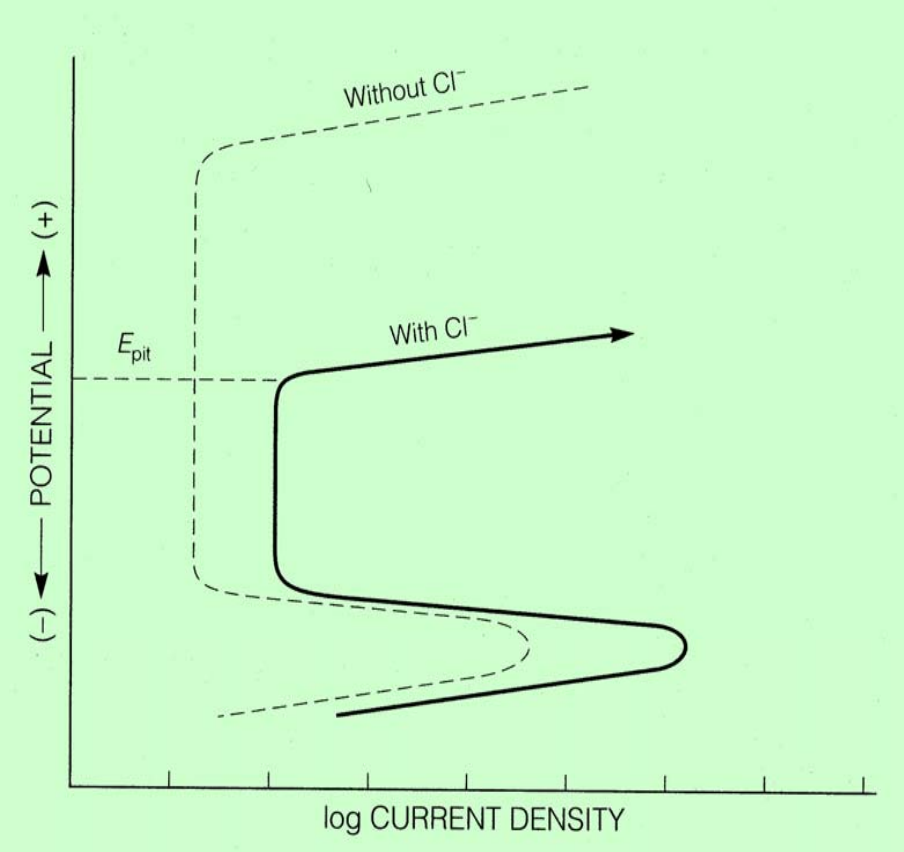
- Dependence of E_{pit} on $[Cl^-]$

$$E_{pit} = A \log [Cl^-] + B$$

$E_{pit} = 0.168 - 0.88 \log [Cl^-]$ (304 stainless steel)
$E_{pit} = 0.05 - 0.124 \log [Cl^-]$ (Al)

- Minimum conc. of [Cl-] necessary for pitting

Alloy	Cl (N)
Fe	0.0003
5.6Cr-Fe	0.017
11.6Cr-Fe	0.069
20 Cr-Fe	0.1
24.5Cr-Fe	1.0
29.4Cr-Fe	1.0
18.6Cr-9.9Ni-Fe	0.1



2) Effects of inhibitor on pitting corrosion

Pitting corrosion depends not only on the $[Cl^-]$, but also on the concentration of unaggressive anions. In general, unaggressive anions produce three different effects on pitting;

i) Increase in E_{pit}

Many anions present in the solution containing Cl^- ions act as inhibitors, ie., SO_4^{2-}, OH^-, CO_3^{2-}, NO^{3-} , all of these anions shifts E_{pit} to more positive values. As the potential of passive metal is shifted in the noble direction, the amount of Cl^- adsorbed on the surface is increased. The anions inhibit the adsorption of Cl^- by a competitive adsorption on the surface of passive film.

The minimum $[Cl^-]$ necessary for pitting in 18-8 stainless steel are given by;

$$\log[Cl^-] = A \log [\text{ inhibitor }] + B$$

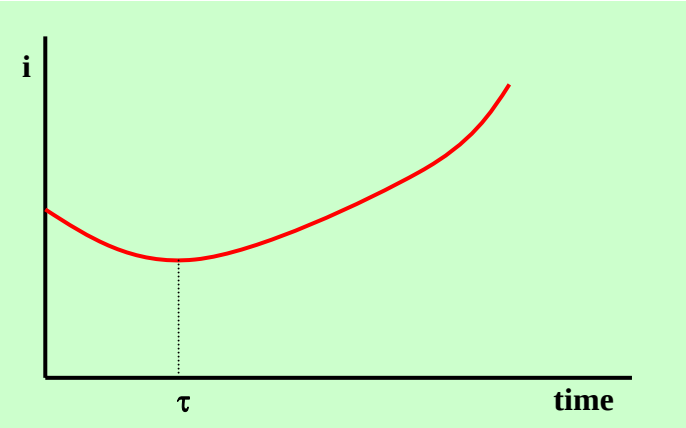
$$\log[Cl^-] = 1.62 \log[OH^-] + 1.84$$
$$\log[Cl^-] = 1.88 \log[NO^{3-}] +1.18$$
$$\log[Cl^-] = 0.85 \log[SO_4^{2-}] -0.05$$
$$\log[Cl^-] = 0.83 \log[ClO^{4-}] - 0.44$$

The efficiency of inhibitor decreased in the order;

$$OH^- < NO^{3-} < SO_4^{2-} < ClO^{4-}$$

ii) Prolong the induction period for pitting

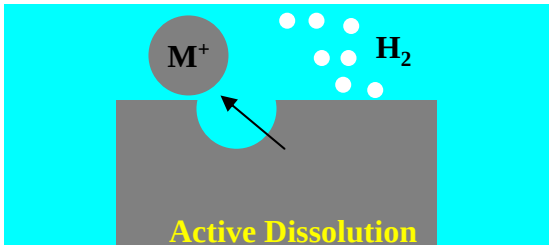
$$1/\tau = k[Cl^-]_x$$



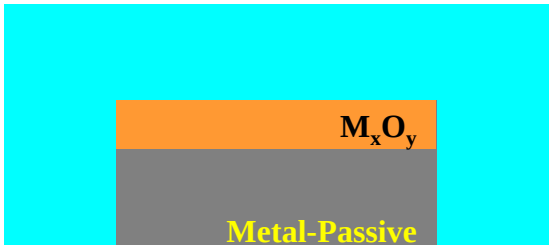
iii) Decrease in the number of pits

Environmental effects on corrosion behavior of stainless steels.

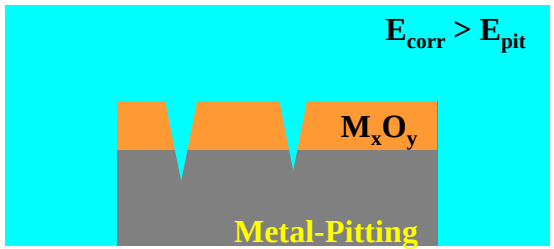
a) Deaerated SO_4^{2-}



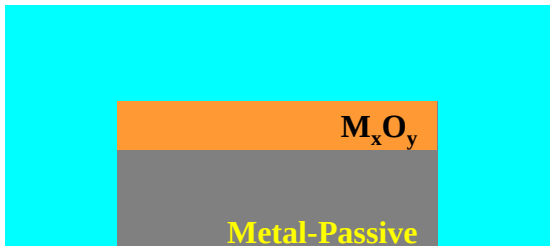
b) Aerated SO_4^{2-}

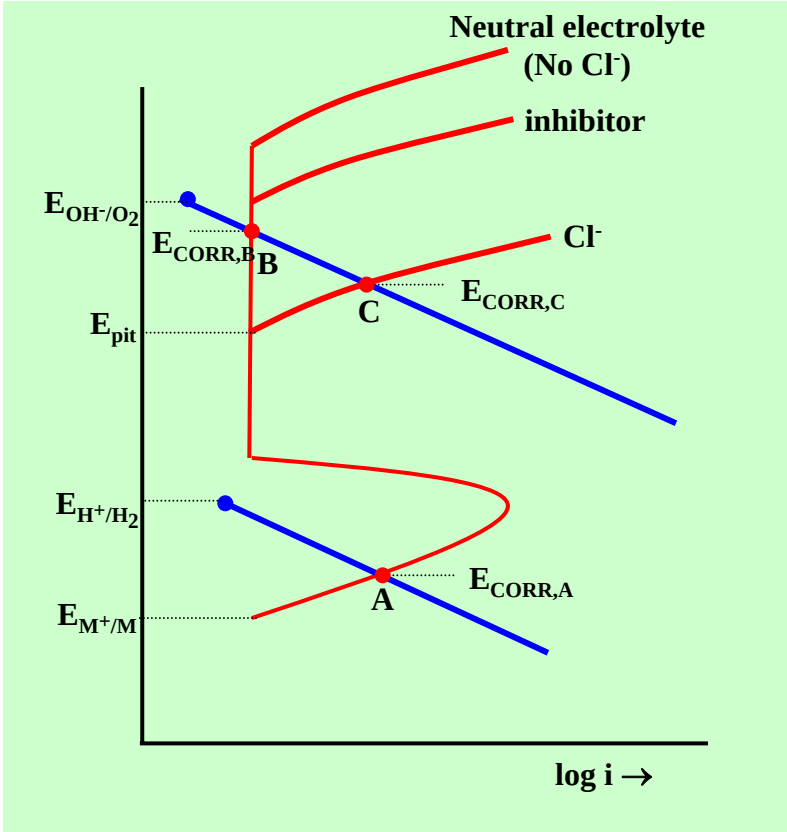


c) Aerated SO_4^{2-} + Cl^-



d) Aerated SO_4^{2-} + Cl^- + inhibitor

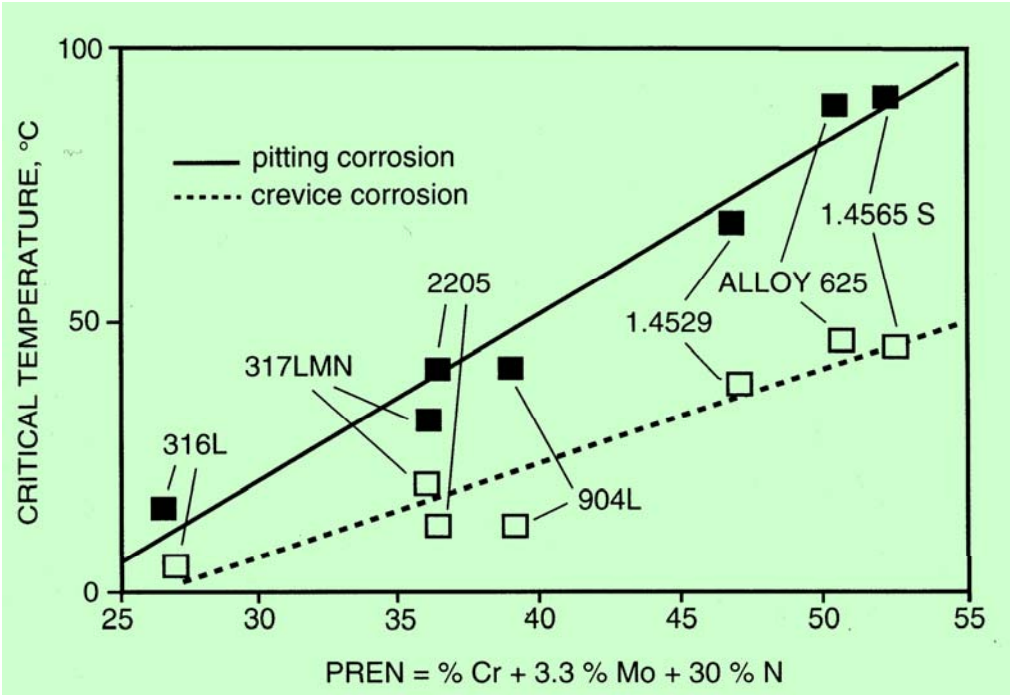




12.5 Effects of alloying element on E_{pit}

The tendency to pitting corrosion of stainless steels decreases as the contents of Cr, Mo and N increases. The addition of Cr to steel changes the nature of the passive film to be amorphous, more homogeneous one with less defects which can not be easily broken down. E_{pit} of austenitic and duplex stainless steels increase in the noble direction with the PRE (pitting resistance equivalent) number;

$$PRE = \%Cr + 3.3\,(\%Mo + 1/2\,\%W) + 16\sim30\,\%N$$



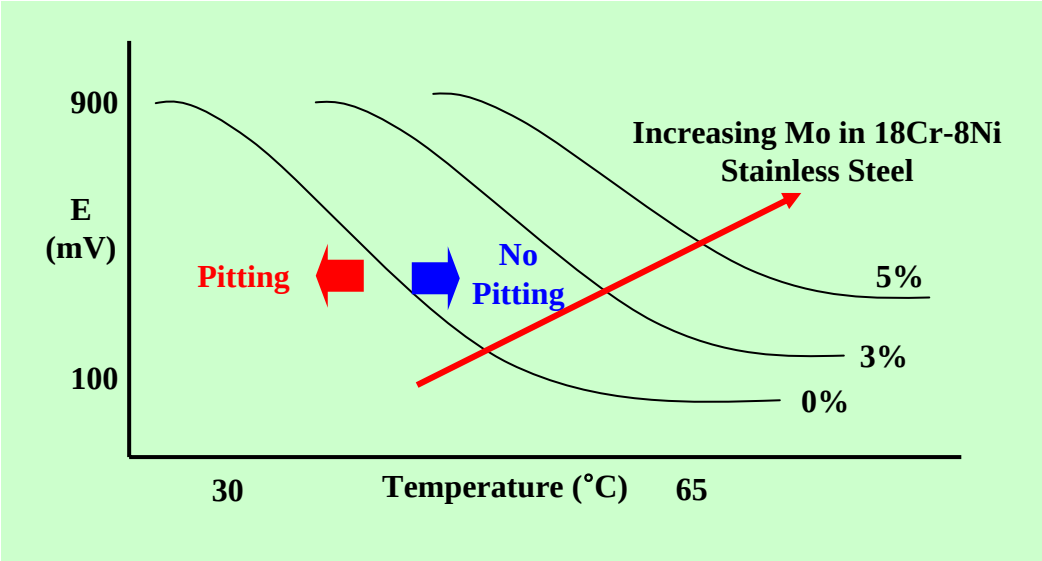
Variation of the critical pitting temperature and critical crevice corrosion temperature.

12. 6 Influence of solution temperature on pitting

Increasing the solution temperature causes E_{pit} to shift in the active direction, indicating an increased tendency toward pitting.

♦ Critical pitting temperature (CPT)

CPT is determined by measuring anodic current of an alloy with increasing the solution temperature either at open circuit or at a selected potential applied to the given alloy. At CPT, the current density increases abruptly. Lower CPT implies greater susceptibility.



12. 7 Growth of Passive Film

1. Experimental observations on the passive films;

• Most of all films grow according to either a logarithmic rate law;

$$L = A + B \ln t$$

or an inverse logarithmic rate law;

$$1/L = C - D \ln t$$

,where L is film thickness, and A, B, C, D are constants.

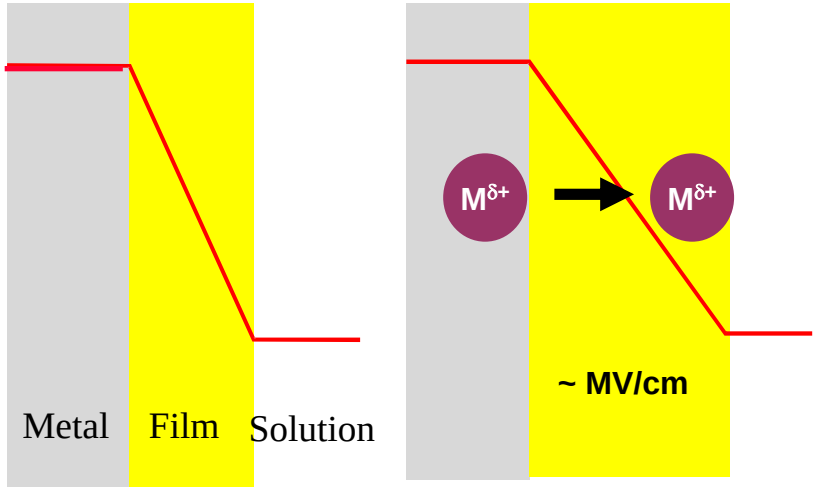
• Many passive films exhibit photoeffects demonstrating that the films have semiconducting properties or highly doped semiconductors.

2. Models on the growth of passive film

A. *High field ion conduction model*

High Field Ion Conduction Model

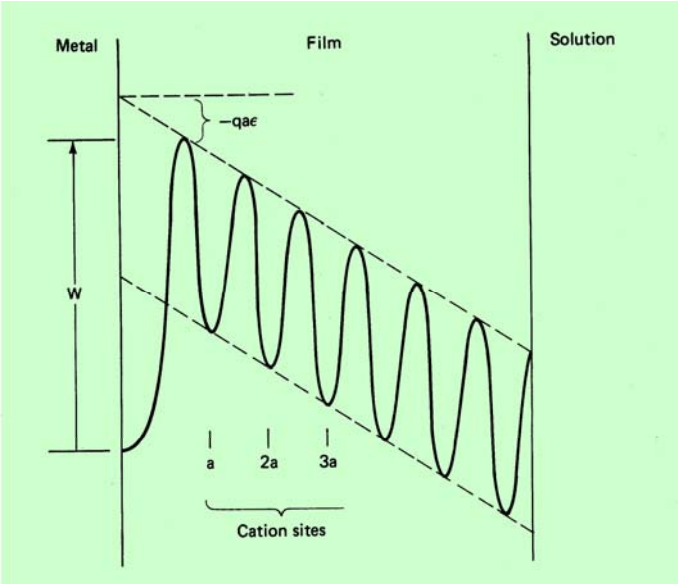
N. Cabrera and N. F. Mott, *Rep. Prog. Phys.*, **12**, 163 (1948).



Before Film Growth After Film Growth

Assumptions;

- The film grows by the transport of M^{z+} ions across the film to the *F/S* interface, where they react with electrolyte.
- The penetration of M^{z+} ions through the film is assisted by the electric field.
- The electric field strength is constant throughout the film and is equal to ϕ_f/L, where ϕ_f is the total potential drop across the film.
- The rate-limiting step for film growth is the emission of M^{z+} ions from the metal into the film.



For the differential film growth rate law;

$$dL/dt = N\Omega\nu \exp\left[(-W + qa\phi_f/2L)/kT\right] \quad \text{.....(1)}$$

where N : number of mobile M^{z+}

Ω : molecular volume per M^{z+}

ν = vibrational frequency

W = activation energy for the entry of M^{z+} into the film

q = charge on the M^{z+}

a = jump distance of M^{z+}

By integration of Eq. (1);

$$1/L = C - D \ln t$$

Fehener and Mott modified the original model by assuming that anion is responsible for film growth, that the rate limiting step is the emission of an anion from the electrolyte into the film at the F/S interface, and that the activation energy for the rate limiting step increases with thickness ($W = W° + \mu L$). Under these assumptions;

$$dL/dt = N\Omega\nu \exp[(-W° - \mu L + qa\phi_f/2L)/kT] \quad \text{.....(2)}$$

The principal objection to this model is that experimental evidence indicates that the interfacial reaction ($O_{oxide} + 2H^+ + 2e^- = H_2O$) is fast so that the emission of an anion from electrolyte to film is unlikely to be the rate limiting step.

B. *Place exchange model (Sato and Cohen)*

From experimental work on the growth of passive film on Fe in borate buffer solutions;

$$i = k' \exp(mV_{app} - Q_t/n) \ldots\ldots\ldots (3)$$

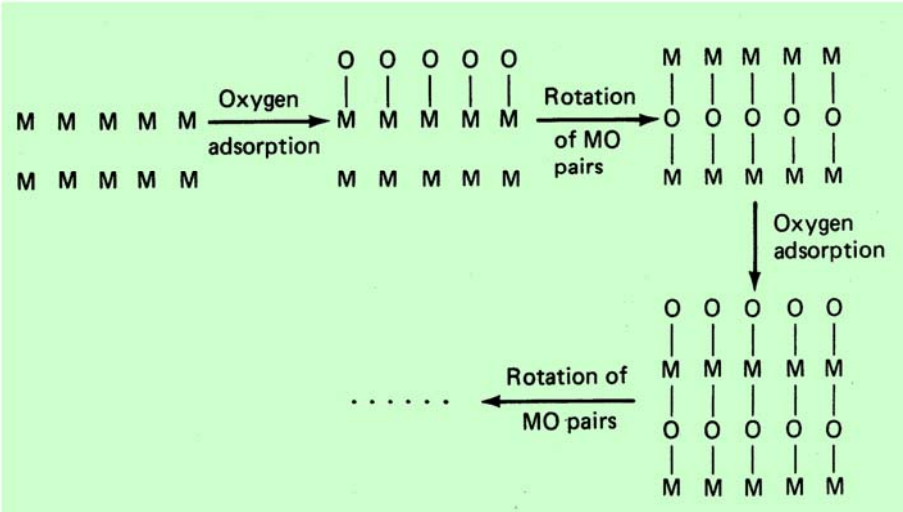
where V_{app} = applied voltage,

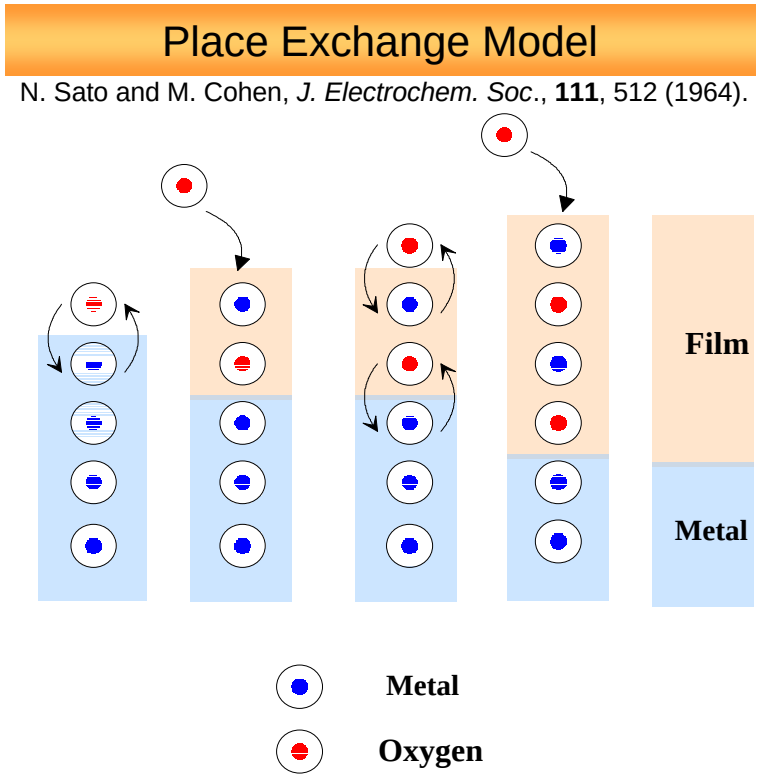
Q_t = the accumulated charge (proportional to L).

Eq(3) can be integrated to yield a logarithmic law;

$$L = A + B \ln(t + t_o) \ldots\ldots\ldots\ldots (4)$$

According this model, film grows by the simultaneous rotation of M-O pairs.





C.*Point Defect Model on Passivity*

(D. D. Macdonald, J. Electrochem. Soc.139 (1992):3424)

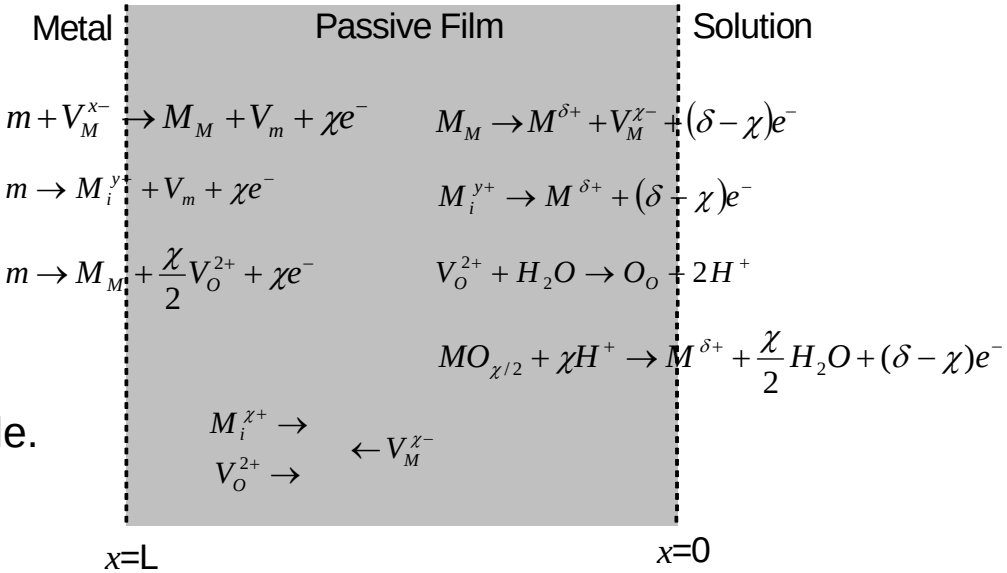
Assumptions

1) A passive film is envisaged as being a highly defective quasicrystalline structure containing cation vacancies, anion vacancies, electrons and holes.
2) Since the electric field across the passive film is extremely high (typically 10^6 V/cm), the film exists on the verge of dielectric breakdown; the field strength is constant and independent of thickness even under potentiostatic conditions

3) The potential difference across the film solution interface is a linear function of the applied potential and the pH of the solution such that

$$\Phi_{f/s} = \Phi^{o}_{f/s} + \alpha V + \beta pH$$

4) The metal/film and film/solution interfaces are under steady-state conditions and reactions at these interfaces are considered to be irreversible.



The sum of reactions (1) and (3) gives;

$$m \rightarrow M^{\delta+}_{(aq)} + \delta e^- \qquad (6)$$ .....dissolution of the metal,

The sum of reaction (2) and (4) gives;

$$m + \chi/2\ H_2O \rightarrow [\ M_M + \chi/2O_O] + \chi H^{\chi+} + \chi e^- \qquad (7)$$

where the $[\ M_M + \chi/2O_O]$ represents the oxide lattice ($MO_{\chi/2}$), and provides for growth of the film into the substrate.

Reactions (1), (2), and (3) are termed lattice-conservative since they do not move the interfaces. On the other hand, reactions (2) and (5) are lattice non-conservative since they result in film formation and dissolution, respectively. Thus, a steady state may be achieved if the rates of reaction (2) and (5) are equal.

Reaction (7) demonstrates that growth of the primary passive film results only from the movement of anion vacancies, whereas the movement of cation vacancies leads to dissolution.

Mathematical analysis of the point defect model yields the following rate law for steady state film growth :

$$\exp(2KL) - 2KL - 1 = 2KA(B - 1)\,t$$

Metal	Passive film	Solution

(1) $m + V_M^{\chi-} \xrightarrow{k_1} M_M + V_m + \chi e^-$

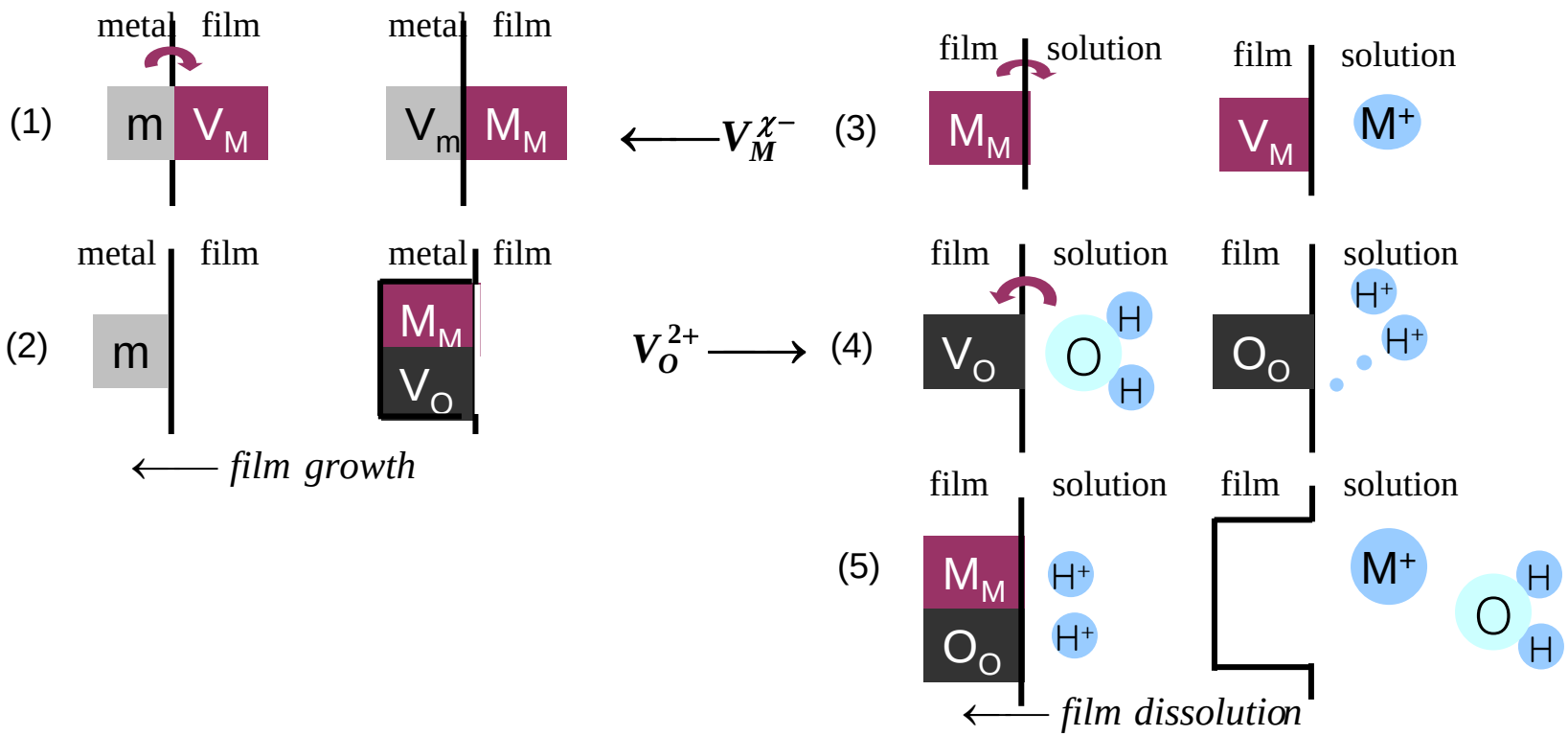
(2) $m \xrightarrow{k_2} M_M + \frac{\chi}{2} V_O^{2+} + \chi e^-$

(3) $M_M \xrightarrow{k_3} M^{\delta+} + V_M^{\chi-} + (\delta - \chi) e^-$

(4) $V_O^{2+} + H_2O \xrightarrow{k_4} O_O + 2H^+$

(5) $MO_{\chi/2} + \chi H^+ \xrightarrow{k_5} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta - \chi) e^-$

$V_O^{2+} \longrightarrow$ $\longleftarrow V_M^{\chi-}$



12. 8 Passivity Breakdown

▶ ***General observations on the passivity breakdown***

• Film breakdown is induced by certain aggressive ions (e. g., Cl-) in solution.

• Breakdown occurs only above a certain critical potential that is related to the activity of the aggressive anion (a_x) by ;

$$E_{pit} = A - B \log a_x$$

• An induction time exists between when conditions conducive to pitting occur and when breakdown actually takes place.

• Breakdown occurs at highly localized sites.

Theories on the passivity breakdown and pit initiation

1) The competitive adsorption theory:

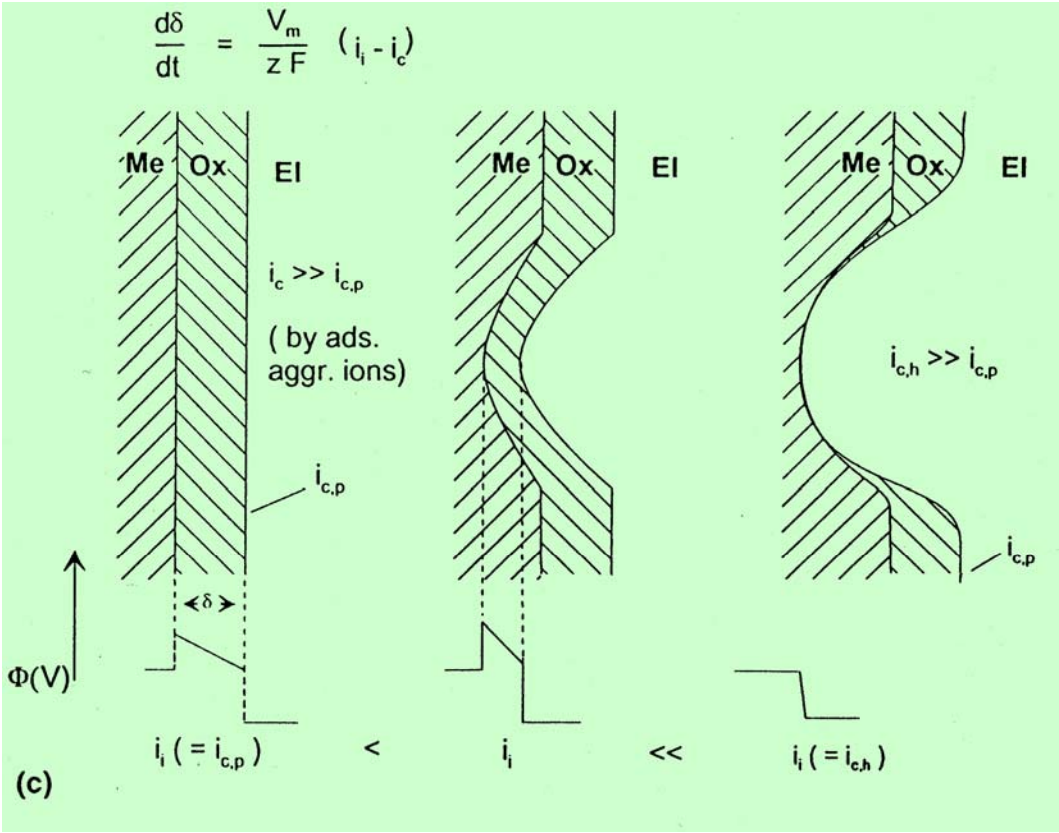
(H. H.Uhilig, J. Electrochem. Soc. 116 (1969): 906. Y. M Kolotyrkin, J. Electrochem. Soc.,108 (1961):209)

O^{2-} and Cl^- anions adsorb onto metal surfaces in a competitive manner. The adsorbsion of O^{2-} results in passivity,whereas that of Cl^- does not. The pits develop on the spots where O^{2-} adsorbed on the metal surface is replaced by Cl^- ions. According to this model, The E_{pit} is the minimum electrode potential at which the Cl^- ions become capable of reversibly replacing the passivating oxygen from film.

2) The complex ion formation theory

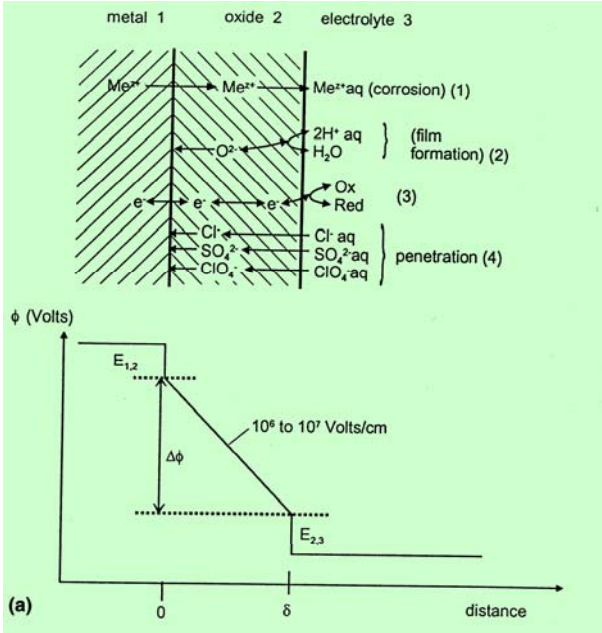
(T. P. Hoar and W. R. Jacob :Nature 216 (1967): 1299)

A small number of Cl- ions jointly adsorb around a cation in the film surface to form complex ion, MCl^{n-} , Once formed, this complex will readily dissolve into solution, leading to local thinning of the film. The higher electric field at this point then causes the rapid transfer of another cation to the surface where it again complexes with the Cl- ions. This “auto-accelerated” dissolution will eventually result in film breakdown.



3) The ion penetration theory

These models generally propose that Cl- incorporates into and migrates through the passive film or through pores or defects in the film to the metal/film interface, resulting in film breakdown.



4) The chemical-mechanical model

(Okada, J. Electrochem. Soc.131(1984):241)

Thin passive films always contain a film pressure (P);

The adsorption of Cl^- on the film greatly reduces the surface tension of the film, which in turn increases the pressure P. When P exceeds some critical value, breakdown occurs.

$$P = P_o + \frac{\delta(\delta - 1)\varepsilon^2}{\gamma\pi} - \frac{Y}{L}$$

P_o : atmospheric pressure
L : film thickness
Y : constant
δ : dielectric constant
γ : surface tension
ε : electric field strength

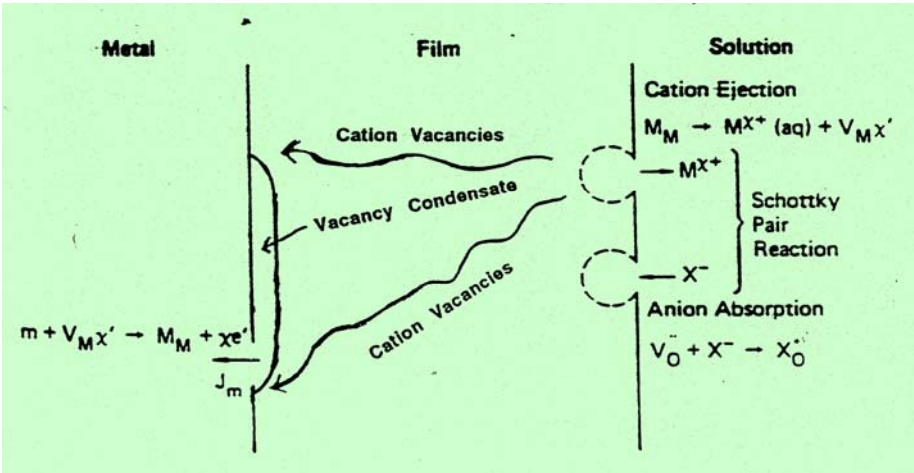
5) The Cation Vacancy Condensation Mechanism

(D. D. Macdonald et al, J. Electrochem. Soc., 128 (1981): 1194).

Based on th point defect model, film breakdown is attributed to the accumulation of cation vacancies at the metal/film interface to form a cation vacancy condensate. When the condensate grows to a critical size, mechanical instability and hence breakdown occurs.

At F/S interface : $\text{Null} \rightarrow V_M^{\chi'} + \left(\frac{\chi}{2}\right) V_{\ddot{O}}$: Schottky-pair type reaction.

$V_{\ddot{O}} + \chi^- \rightarrow \chi_{\dot{O}}$: absorption of an aggressive ion into $V_{\ddot{O}}$



Metal	Passive film	Solution

(1) $m + V_M^{\chi-} \xrightarrow{k_1} M_M + V_m + \chi e^-$

(2) $m \xrightarrow{k_2} M_M + \frac{\chi}{2} V_O^{2+} + \chi e^-$

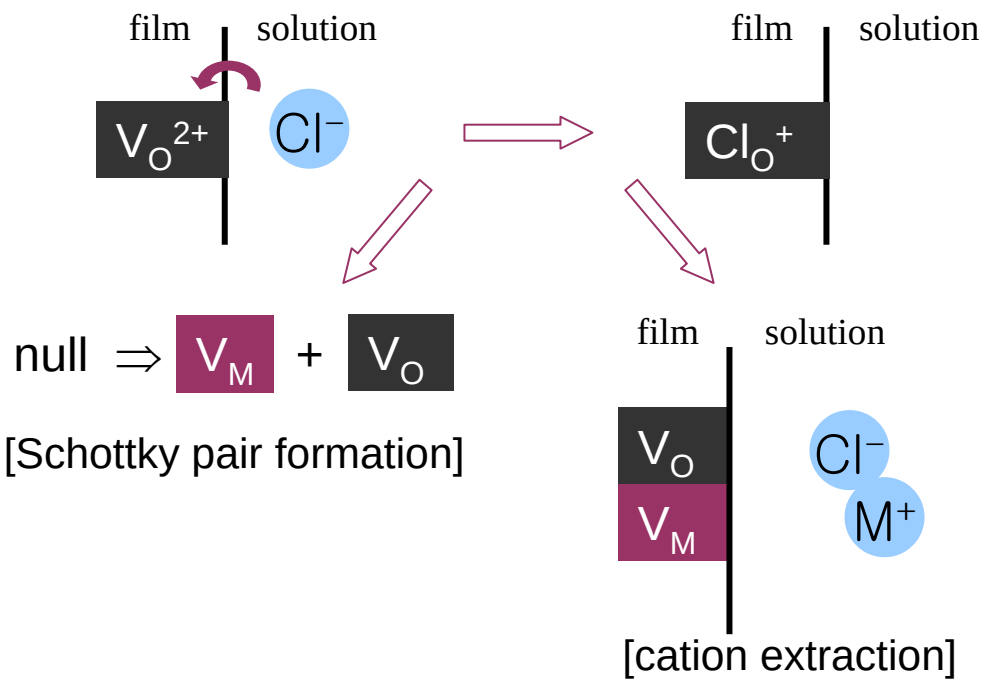
(3) $M_M \xrightarrow{k_3} M^{\delta+} + V_M^{\chi-} + (\delta - \chi) e^-$

(4) $V_O^{2+} + H_2O \xrightarrow{k_4} O_O + 2H^+$

(5) $MO_{\chi/2} + \chi H^+ \xrightarrow{k_5} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta - \chi) e^-$

$\boldsymbol{V_O^{2+}} \longrightarrow$ $\boxed{\longleftarrow \boldsymbol{V_M^{\chi-}}}$

- **Role of Cl^- ion**



Cl^- occupies the oxygen vacancy site in the film.

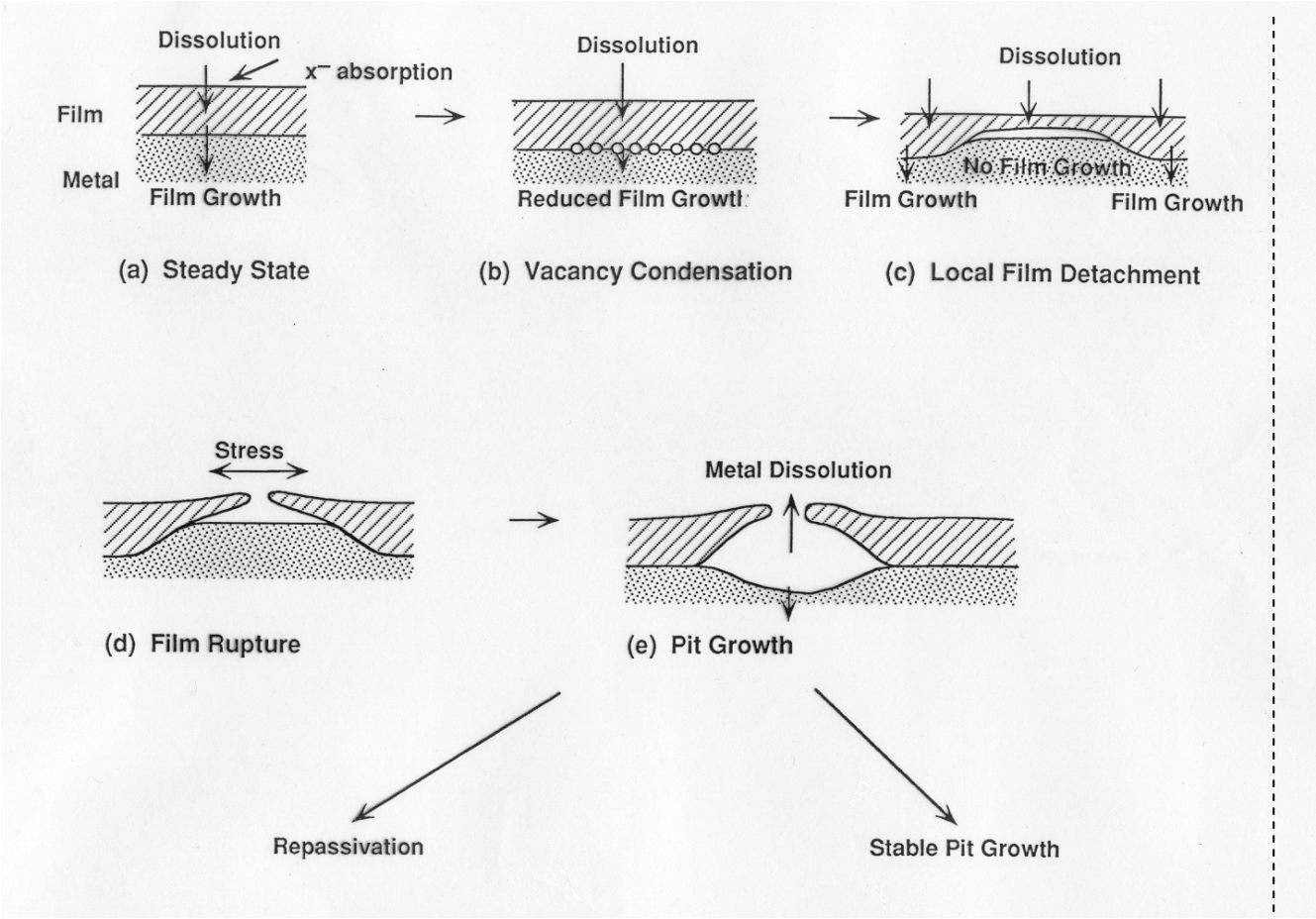
Decrease in $[V_O^{2+}]$

Possible two side reactions to increase $[V_O^{2+}]$

$[V_O^{2+}]$

Excess V_M : $[V_M]$ ↑

- **Breakdown mechanism**



Steady state

$R_{film\ growth} = R_{dissolution}$

$[V_M]$ inceased by Cl^-

Vacancy condensation

$R_{generation} >> R_{annihilation}$

Film detachment by void formation

Film rupture and Pit growth

The most important factor : Concentration and flux of V_M

6) A model on the structure and breakdown of passive films on stainless steels
(G. Okamoto, Corros Sci., 13 (1973): p. 471)

- This model assumes that the passive film is a hydrated oxide film having a gel-like amorphous structure.
- Types of bond ;
  H_2O-M-H_2O, OH-M-OH, O-M-O ;
  the amount of bound water decreases with increasing passivation potential.
- The model also explains pitting; chloride ions adsorb onto the surface of the film and replace the water molecules. The replacement by chloride ions at the bridge position results in the formation of a soluble metal chloride complex through which metal ions are removed from the oxide film.

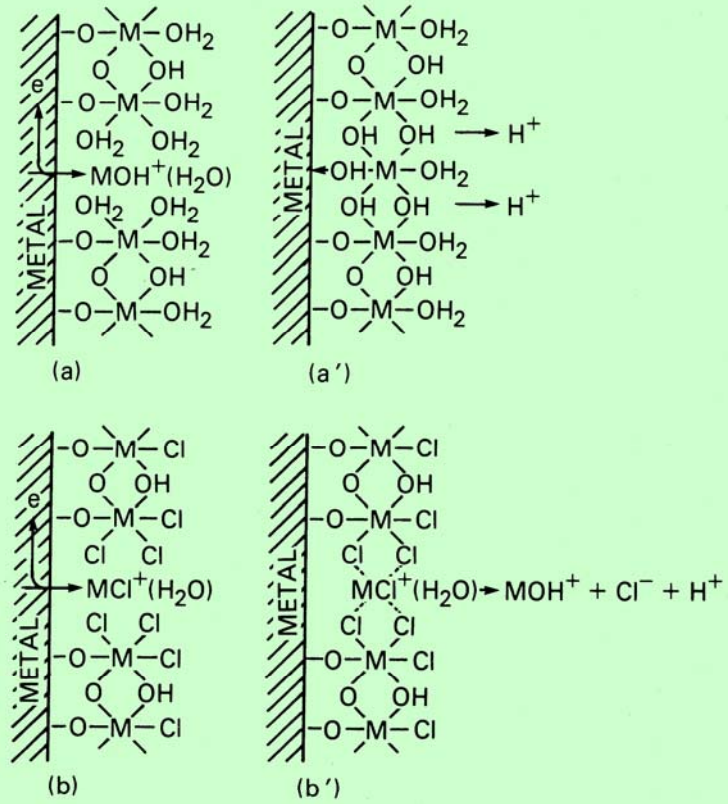
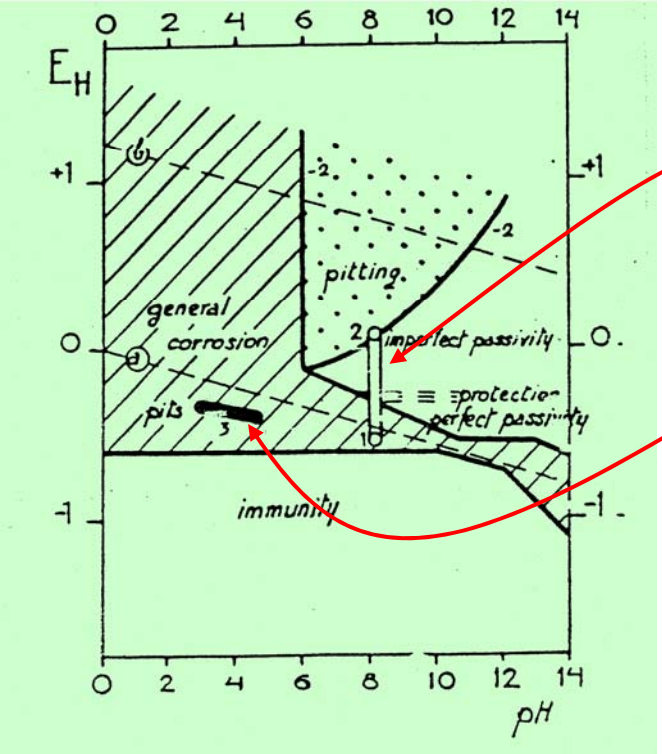
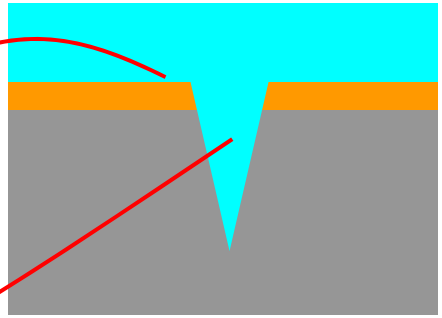
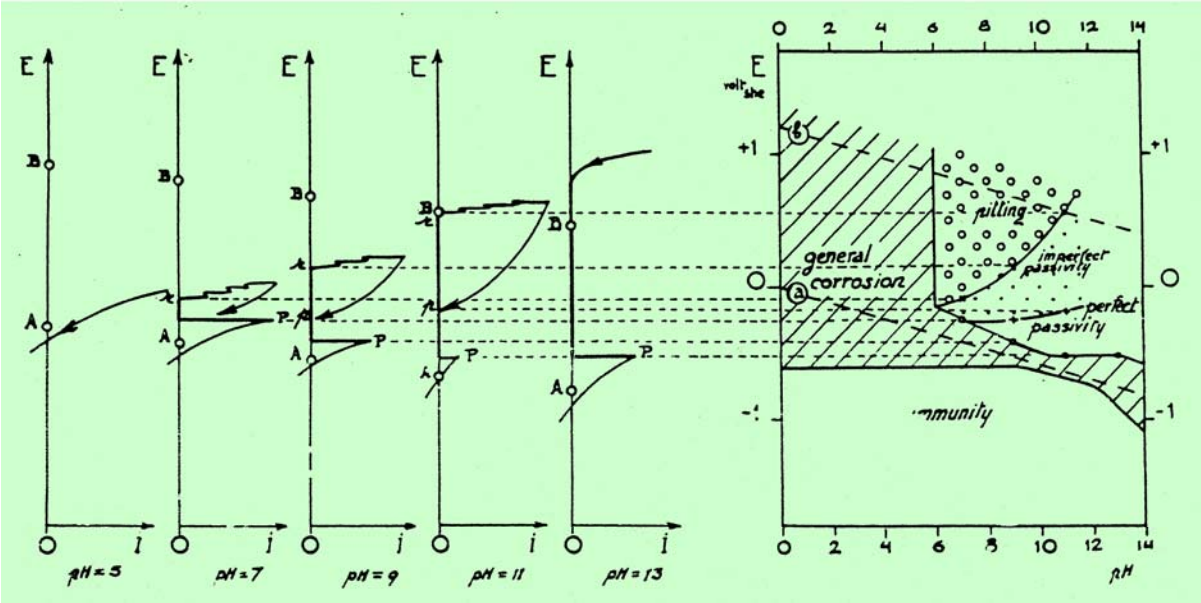


Figure 3.7 Metal ions dissolved through an undeveloped part of the film (a) are captured to form a film (a′) resulting from bridging with OH groups. Chloride ions replacing water molecules (b) prevent the bridging reaction (b′), resulting in breakdown of the film. (After Reference 17.)

12. 8 Critical potential for pitting on Pourbaix diagram