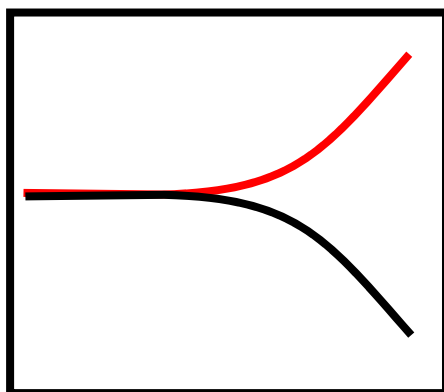




# 電気化学会関西支部 第 51 回電気化学講習会 電気化学の基礎と新しいアプローチ

## 2. 分極曲線の考え方～腐食, ナトリウムイオン電池, 電気二重層キャパシタ, 燃料電池～ (その1)

(産業技術総合研究所) 倉谷健太郎  
(京都大学) 深見一弘  
(大阪大学) 土谷博昭  
(鳥取大学) 薄井洋行  
(大阪公立大学) 知久昌信  
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This supplementary material is the presentation file provided at the 51st Electrochemistry Workshop held by Kansai in response to the comprehensive paper in *Electrochemistry*, **90(10)**, 102003 (2022) <https://doi.org/10.5796/electrochemistry.22-66085> entitled,

### Electrochemical Polarization Part 1: Fundamentals and Corrosion

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# Electrochemical Polarization Part 1: Fundamentals and Corrosion

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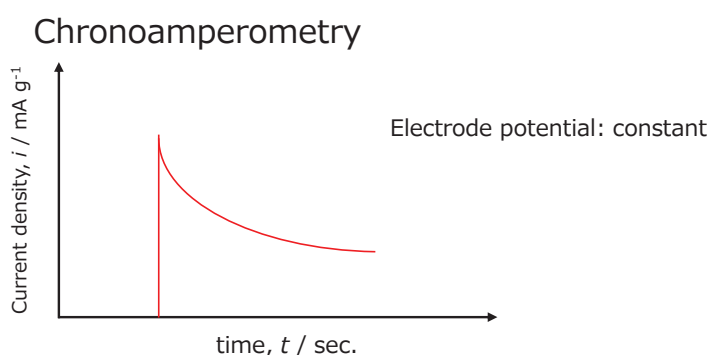
<sup>c</sup> Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka, 565-0871, Japan

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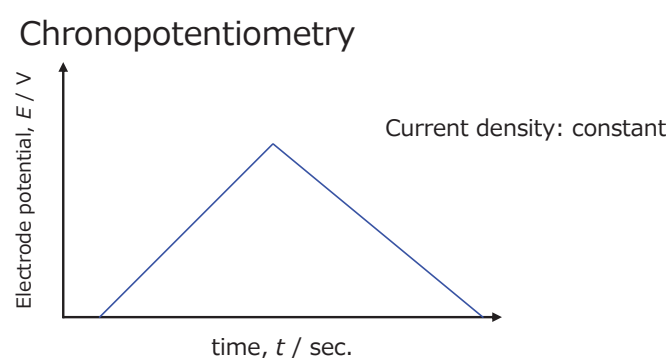
<sup>e</sup> Graduate School of Engineering, Osaka Metropolitan University, 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka, 599-8531, Japan

## Polarization measurements

The term of “**chrono**” is descended from “**chronos**”, which means “**time**” in Greek.



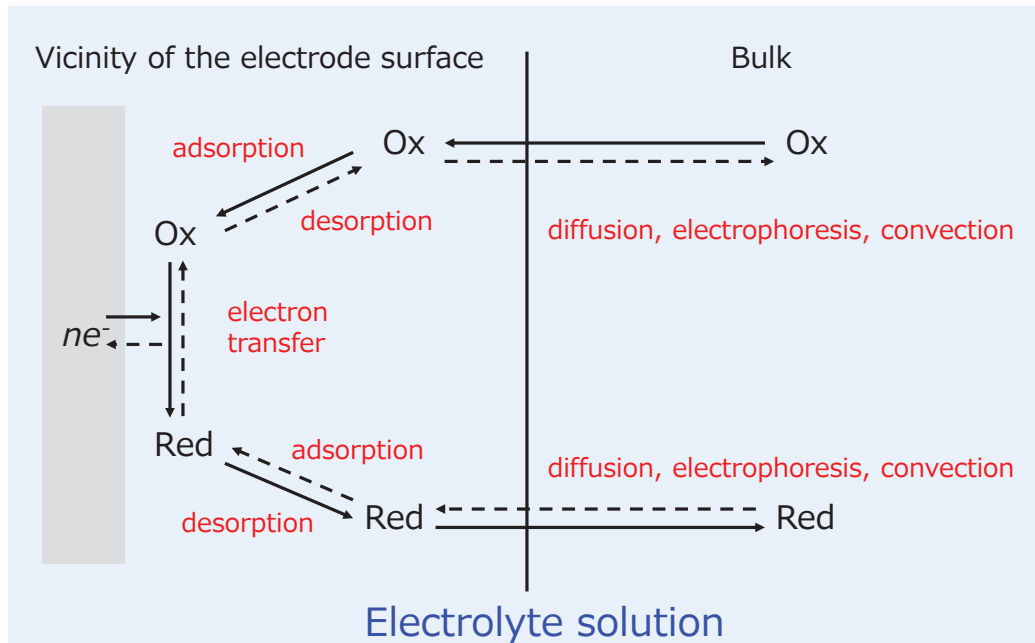
Ex.) Corrosion reaction  
Metal finishing



Ex.) Charge/discharge reaction

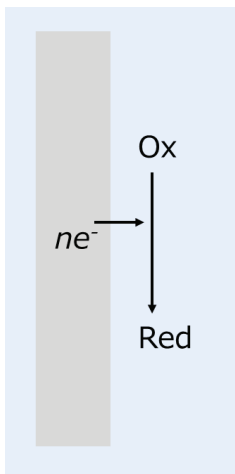
**Understanding the correlation between electrode potential and current density is significant to analyze the results obtained from polarization measurement.**

# Model of electrode reaction process



## Current

$\text{Ox} + ne^- \rightarrow \text{Red}$  (Electrochemical reaction under a constant current,  $I$  (A), for  $t$  (s))



**Product mass of Red (mol):**  $N_{\text{Red}} (\text{mol}) = It/nF = Q/nF$

$n$ : stoichiometric coefficient of electrons in electrochemical reaction  
 $F$ : Faraday constant ( $96500 \text{ C mol}^{-1}$ )  
 $Q$ : electric charge generated by the reaction

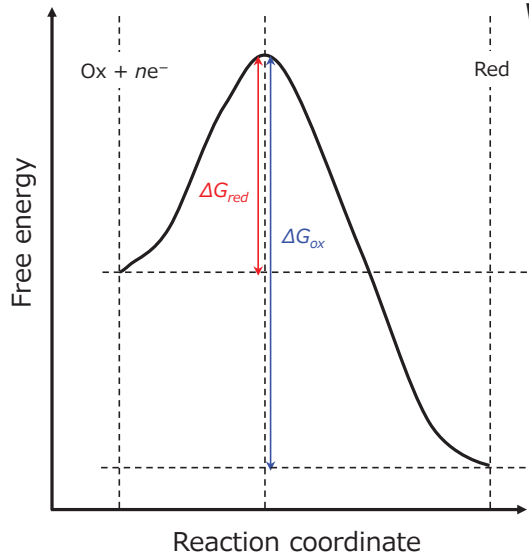
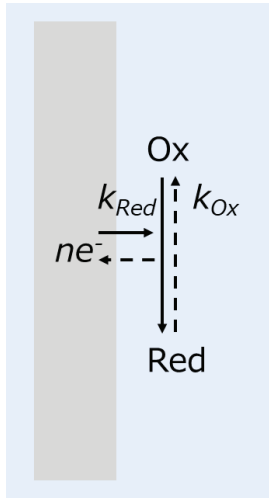
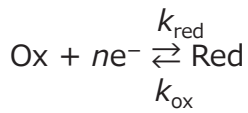
**Reaction rate of Red ( $\text{mol s}^{-1}$ ):**  $v_t = dN/dt = I/nF$

**Reaction rate of Red ( $\text{mol s}^{-1}$ ):**  $v_t = iS/nF$

$I = iS$ ,  $i$ : current density,  $S$ : electrode square

**Reaction rate can be controlled by changing the current density.**

# Current-potential curve



$$v_{\text{red}} = A c_{\text{ox}} \exp(-\Delta G_{\text{red}}/RT) = k_{\text{red}} c_{\text{ox}}$$

$$v_{\text{ox}} = A c_{\text{red}} \exp(-\Delta G_{\text{ox}}/RT) = k_{\text{ox}} c_{\text{red}}$$

$A$ : frequency factor

$c_{\text{ox}}$ : concentration of the reactant near the electrode

$c_{\text{red}}$ : concentration of the product near the electrode

$\Delta G_{\text{red}}$ : activation energy of the reduction reaction

$\Delta G_{\text{ox}}$ : activation energy of the oxidation reaction

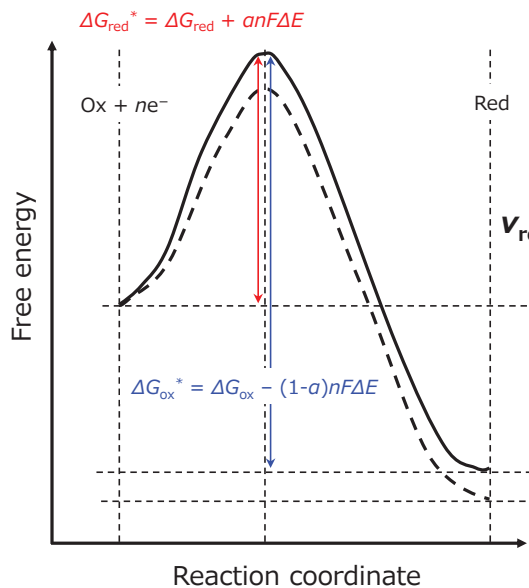
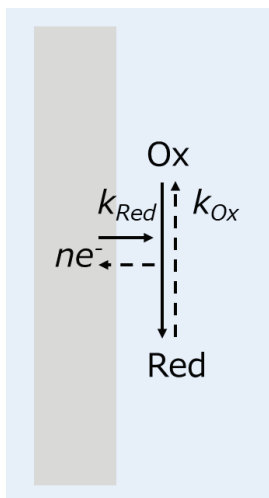
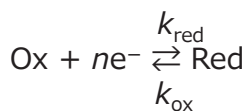
$R$ : molar gas constant

$T$ : absolute temperature

$k_{\text{red}}$ : reaction rate constant of the reduction reaction

$k_{\text{ox}}$ : reaction rate constant of the oxidation reaction

# Current-potential curve



When the potential difference ( $\Delta E$ ) exists at the electrode/electrolyte interface,

$$\Delta G_{\text{red}}^* = \Delta G_{\text{red}} + anF\Delta E$$

$a$ : transfer coefficient ( $0 < a < 1$ )

$$v_{\text{red}} = A c_{\text{ox}} \exp(-\Delta G_{\text{red}}/RT) = k_{\text{red}} c_{\text{ox}}$$

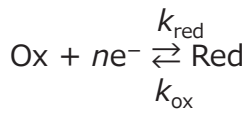
$$v_{\text{red}} = A c_{\text{ox}} \exp(-\Delta G_{\text{red}}^*/RT)$$

$$= A c_{\text{ox}} \exp(-(\Delta G_{\text{red}} + anF\Delta E)/RT)$$

$$= A c_{\text{ox}} (\exp(-\Delta G_{\text{red}}/RT) \times \exp(-anF\Delta E)/RT)$$

$$= k_{\text{red}} c_{\text{ox}} \exp(-anF\Delta E)/RT$$

# Current-potential curve



$$v_{\text{red}} = k_{\text{red}} c_{\text{ox}} \exp(-anF\Delta E)/RT$$

This equation can also be edited to current density by multiplying Faraday constant.

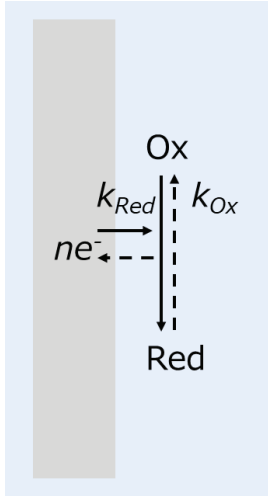
$$\begin{aligned} i_{\text{red}} &= Fv_{\text{red}} & i_{\text{ox}} &= Fv_{\text{ox}} \\ &= Fk_{\text{red}}c_{\text{ox}}\exp(-anF\Delta E)/RT & &= Fk_{\text{ox}}c_{\text{red}}\exp((1-a)nF\Delta E)/RT \end{aligned}$$

Under the equilibrium state,  $i_{\text{red}} = i_{\text{ox}}$

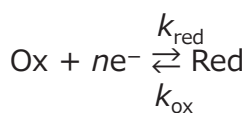
$$i_0 = i_{\text{red}} = i_{\text{ox}} \quad (\text{exchange current density})$$

$$= Fk_{\text{red}}c_{\text{ox}}\exp(-anF\Delta E_{\text{eq}})/RT$$

$$= Fk_{\text{ox}}c_{\text{red}}\exp((1-a)nF\Delta E_{\text{eq}})/RT$$



# Current-potential curve



In case the equilibrium state gets out of balance, current flows to the external circuit ( $i_{\text{red}} \neq i_{\text{ox}}$ ).

Also, we call the potential difference under this situation as overpotential ( $\eta$ ) which means the difference of the electrode potential from the equilibrium potential.

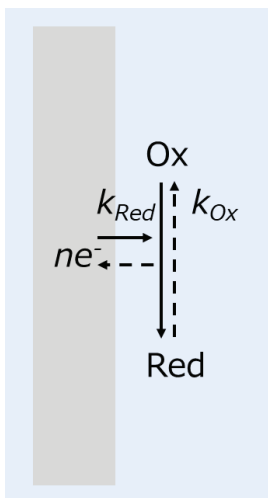
$$i = i_{\text{red}} - i_{\text{ox}}$$

$$= Fk_{\text{red}}c_{\text{ox}}\exp(-anF(\Delta E_{\text{eq}} + \eta)/RT)$$

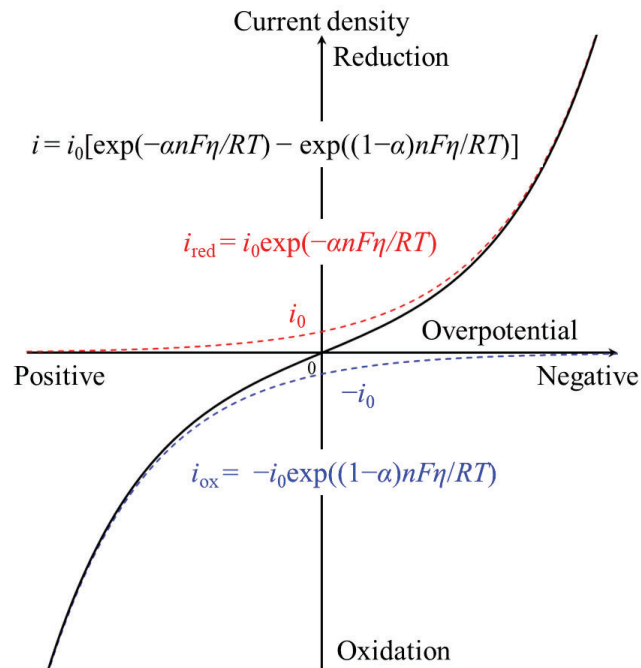
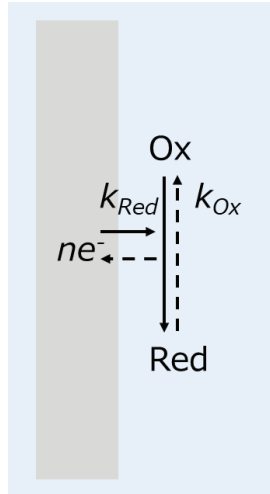
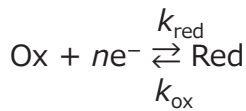
$$- Fk_{\text{ox}}c_{\text{red}}\exp((1-a)nF(\Delta E_{\text{eq}} + \eta)/RT)$$

$$= i_0[\exp(-anF\eta/RT) - \exp((1-a)nF\eta/RT)]$$

## Butler-Volmer equation



# Current-potential curve based on Butler-Volmer equation



## Current-potential curve

In case of  $|\eta| < 5 \text{ mV}$

$$i = i_0 [\exp(-anF\eta/RT) - \exp((1-a)nF\eta/RT)]$$

Taylor expansion

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots, \quad -\infty < x < \infty$$

$$e^x = 1 + x$$

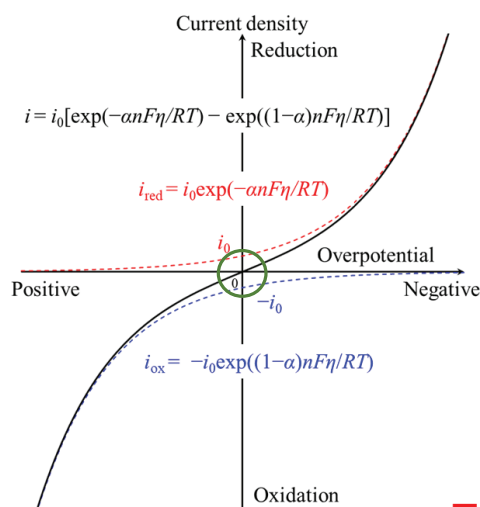
$$i = i_0 [1 + (-anF\eta/RT) - (1 + (1-a)nF\eta/RT)]$$

$$= i_0 (nF\eta/RT)$$

$$\eta = -(RT/i_0 nF) i$$

$$-\eta/i = RT/i_0 nF$$

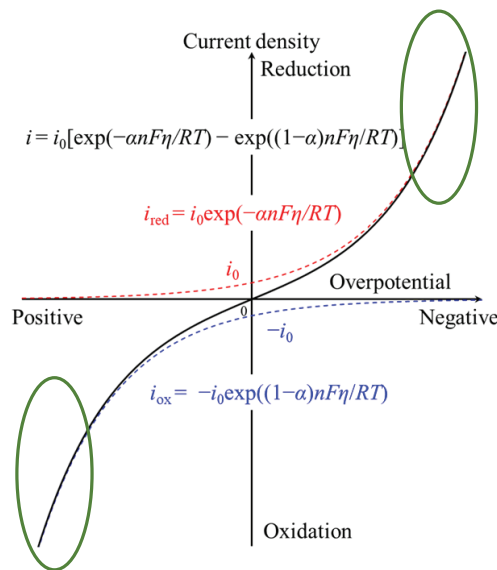
$$= R_{\text{ct}} \text{ (} R_{\text{ct}} \text{: charge transfer resistance)}$$



# Current-potential curve

In case of  $|\eta| > 70 \text{ mV}$

$$i = i_0 [\exp(-anF\eta/RT) - \exp((1-a)nF\eta/RT)]$$



(i)  $\eta < -70 \text{ mV}$  (the term  $i_{ox}$  is negligible.)

$$i = i_0 \exp(-anF\eta/RT)$$

$$\eta = (RT \ln i_0) / anF - (RT \ln i) / anF$$

$$= 2.303RT \log i_0 / anF - 2.303RT \log i / anF$$

(ii)  $\eta > +70 \text{ mV}$  (the term  $i_{red}$  is negligible.)

$$i = -i_0 \exp((1-a)nF\eta/RT) = |i_0| \exp((1-a)nF\eta/RT)$$

$$\eta = -(RT \ln i_0) / (1-a)nF + (RT \ln i) / (1-a)nF$$

$$= -2.303RT \log i_0 / (1-a)nF - 2.303RT \log i / (1-a)nF$$

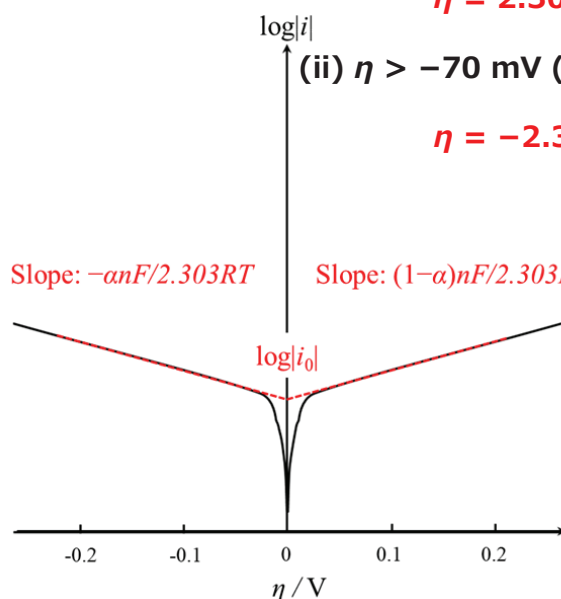
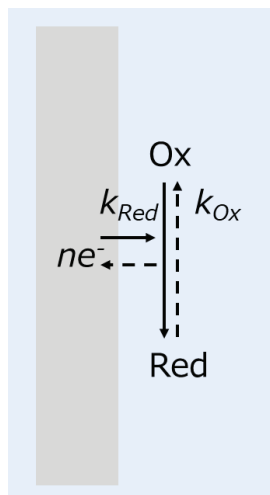
## Tafel plot

(i)  $\eta < -70 \text{ mV}$  (the term  $i_{ox}$  is negligible.)

$$\eta = 2.303RT \log i_0 / anF - 2.303RT \log i / anF$$

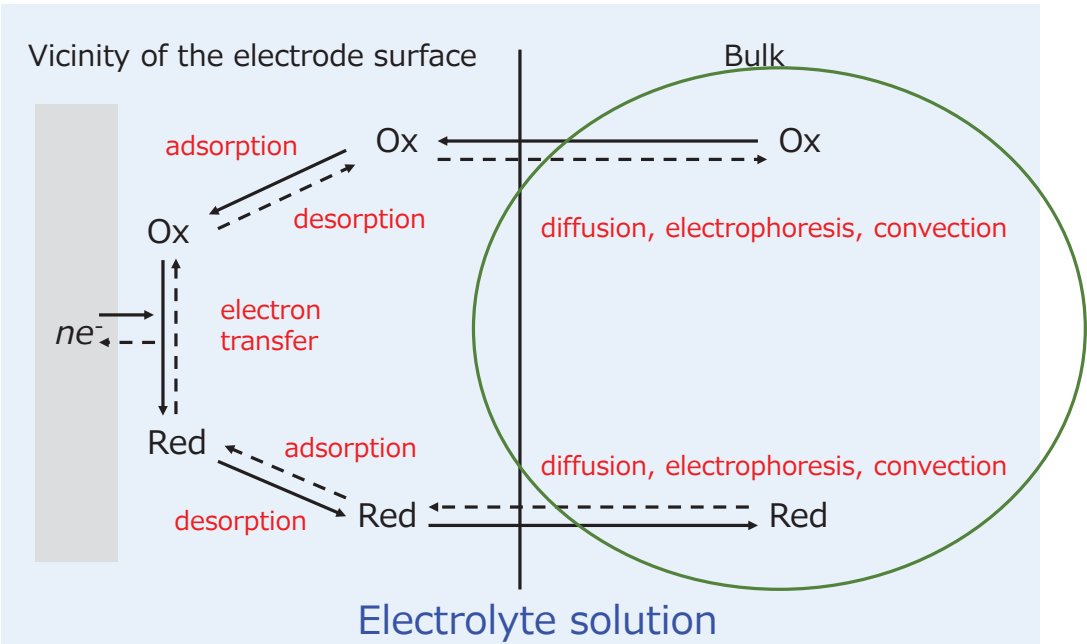
(ii)  $\eta > -70 \text{ mV}$  (the term  $i_{ox}$  is negligible.)

$$\eta = -2.303RT \log i_0 / (1-a)nF - 2.303RT \log i / (1-a)nF$$

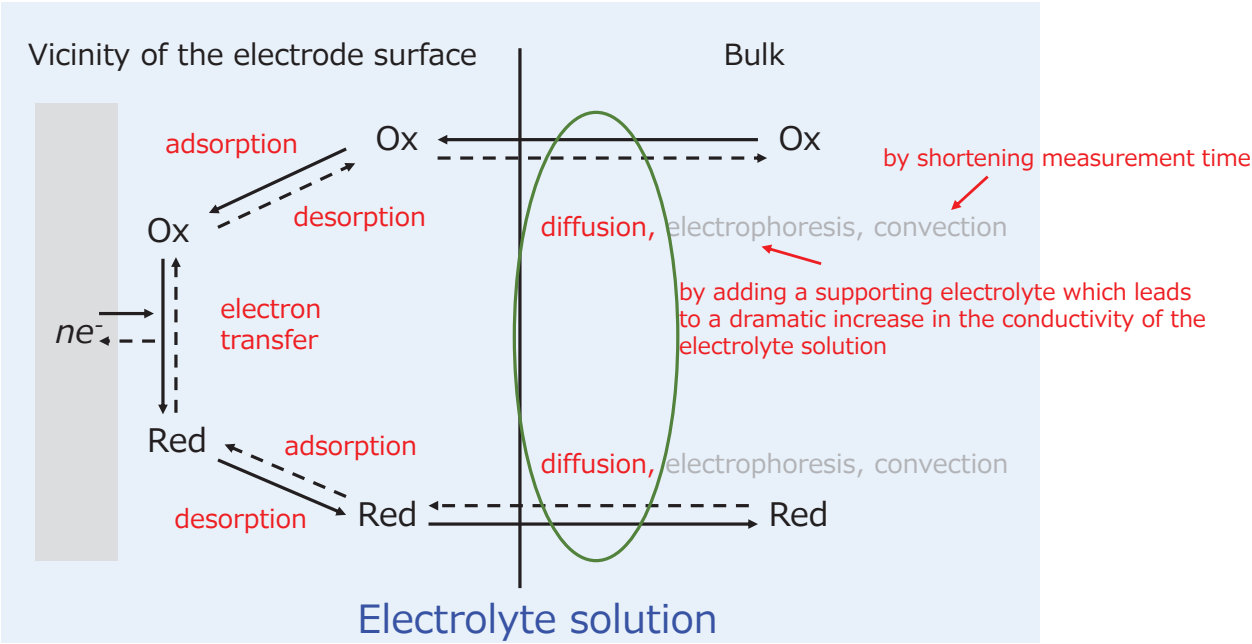


Tafel equation ( $\eta = a \pm b \log i$ )

# Model of electrode reaction process

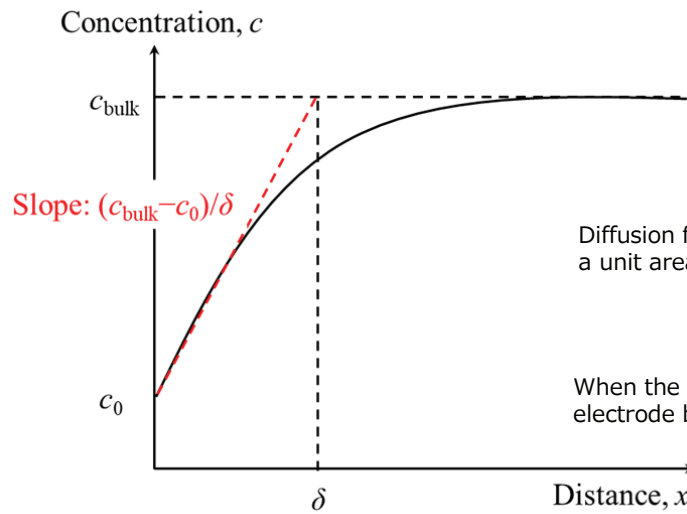
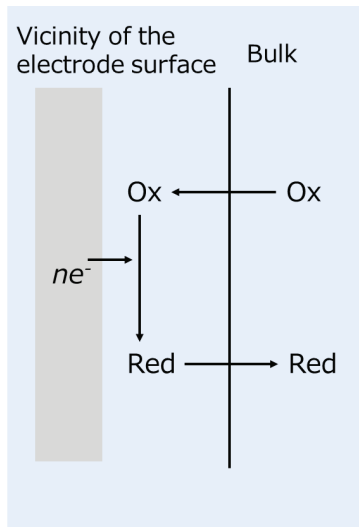


# Model of electrode reaction process





# Mass transfer



## Fick's first law

$$J = -D(dc_{\text{bulk}}/dx)$$

$C_0$  : concentration of the reactant at  $x=0$

$D$  : diffusion constant

$J$  : diffusion flux

$$J = -D(c_{\text{bulk}} - c_0)/\delta$$

Diffusion flux is mole number that passes through a unit area of cross-section in a unit time

$$i = -nFD(c_{\text{bulk}} - c_0)/\delta$$

When the concentration of the reactant near the electrode becomes 0 ( $C_0 = 0$ )

$$i = -nFD(c_{\text{bulk}})/\delta$$

Diffusion-limiting current density

# Electrochemical Polarization Part 1: Fundamentals and Corrosion

Electrochemical Polarization in Fundamental Corrosion Research

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Hiroyuki Usui,<sup>d</sup> Masanobu Chiku,<sup>e</sup> Shin-ichi Yamazaki<sup>a</sup>

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## Equilibrium and Steady State

### Equilibrium

Consider a half-cell reaction



The equilibrium potential is expressed by the Nernst equation.

$$E_{\text{M}^{2+}/\text{M}} = E_{\text{M}^{2+}/\text{M}}^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{\text{M}^{2+}}}$$

### Steady state

Two half-cell reactions are coupled.



# Equilibrium and Steady State

## Steady state

Equilibrium potentials of the two reactions

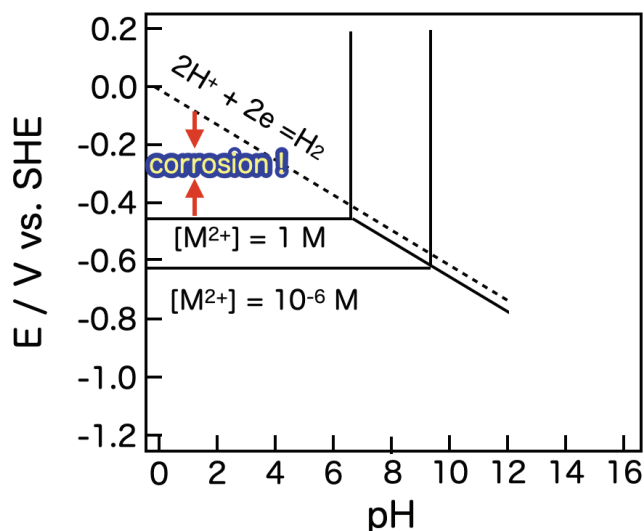
$$E_{M^{2+}/M} = E_{M^{2+}/M}^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{M^{2+}}}$$

$$E_{H^{+}/H_2} = E_{H^{+}/H_2}^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{H^{+}}^2}$$

The corrosion of M occurs when the *emf* of the coupled reaction is positive ( $\Delta G$  is negative).

Potential-pH diagrams are helpful to judge thermodynamically whether a corrosion reaction of interest occurs or not.

## Potential-pH diagram (Pourbaix diagram)

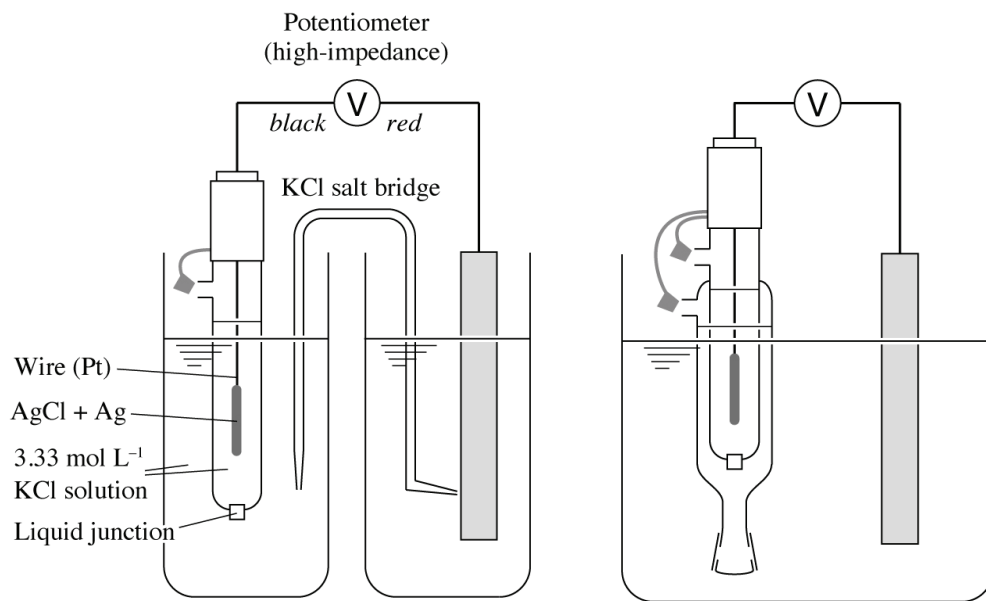


Potential-pH diagram gives information whether the corrosion thermodynamically occurs or not.

To understand the corrosion quantitatively, evaluation by stationary polarization is necessary.

## Electrochemical measurements

### Measurement for corrosion potential

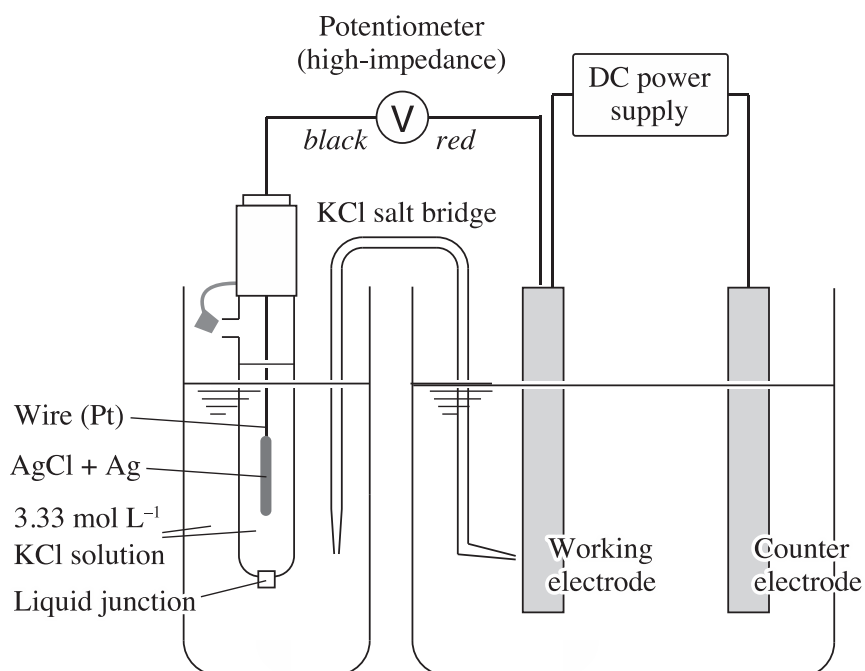


When the contamination of Cl<sup>-</sup> is not allowed, a double-junction type reference electrode or a reference electrode without Cl<sup>-</sup> should be used.

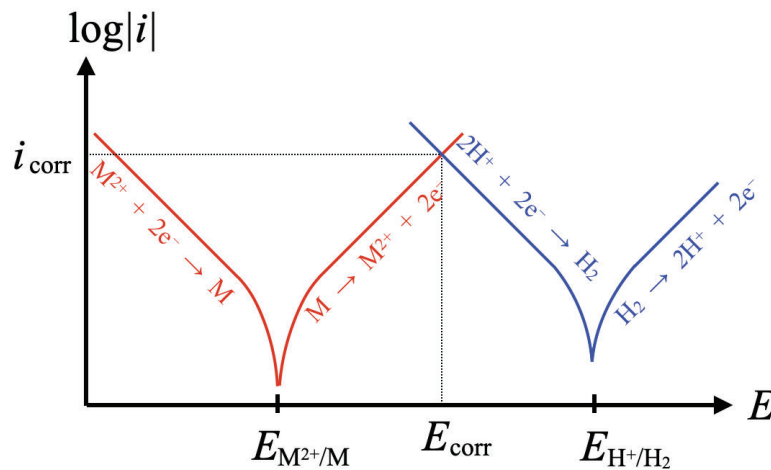
(ex. Hg|Hg<sub>2</sub>SO<sub>4</sub> in an acidic solution and Hg|HgO in an alkaline solution)

## Electrochemical measurements

### Measurement for stationary polarization



## Stationary polarization curves

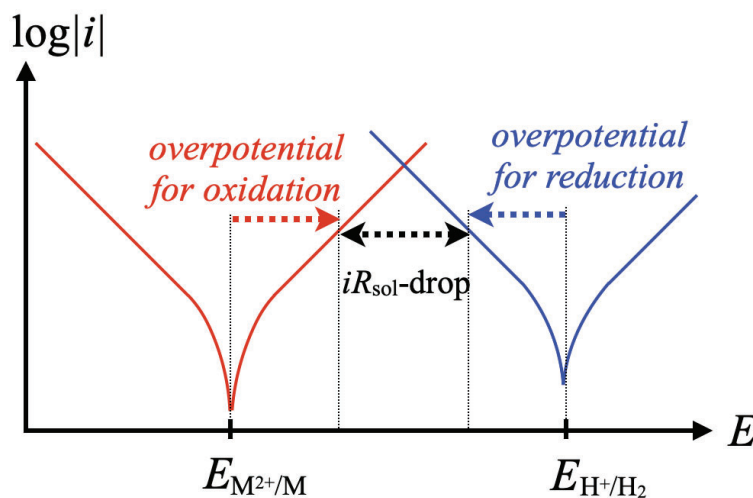


The current density for the oxidation of M is equal to that for the reduction of  $H^+$  to  $H_2$  at the potential denoted as  $E_{corr}$ .

$E_{corr}$  is the corrosion potential, while  $i_{corr}$  is the corrosion current density.

## Effect of $iR_{sol}$ -drop in solution on corrosion rate

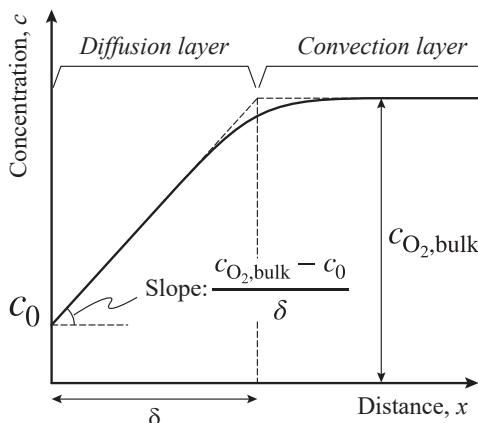
The  $iR_{sol}$ -drop in the test solution must be considered to discuss corrosion behavior quantitatively.



The overpotential for the oxidation of M decreases when the conductivity of the test solution is not high.

## Effect of mass-transfer on corrosion rate

In corrosion reactions, the reduction reaction can be the oxygen reduction to water.

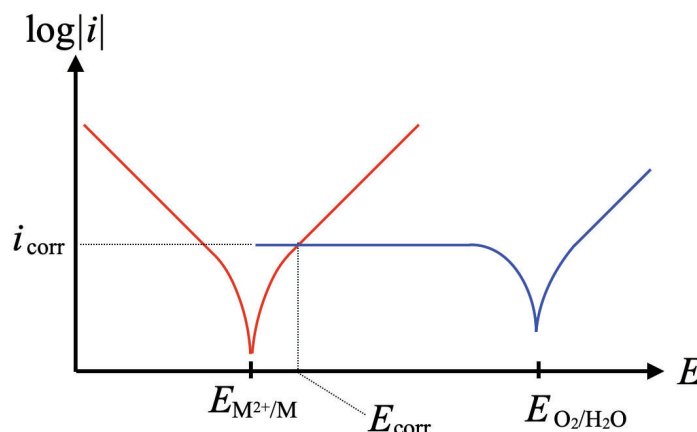


The concentration of dissolved oxygen is low.

The oxygen reduction takes place under diffusion-limited condition.  
(expressed by the Cottrell equation)

$$|i_{O_2,diff}| = \frac{4FD_{O_2}c_{O_2,bulk}}{\delta}$$

## Effect of mass-transfer on corrosion rate

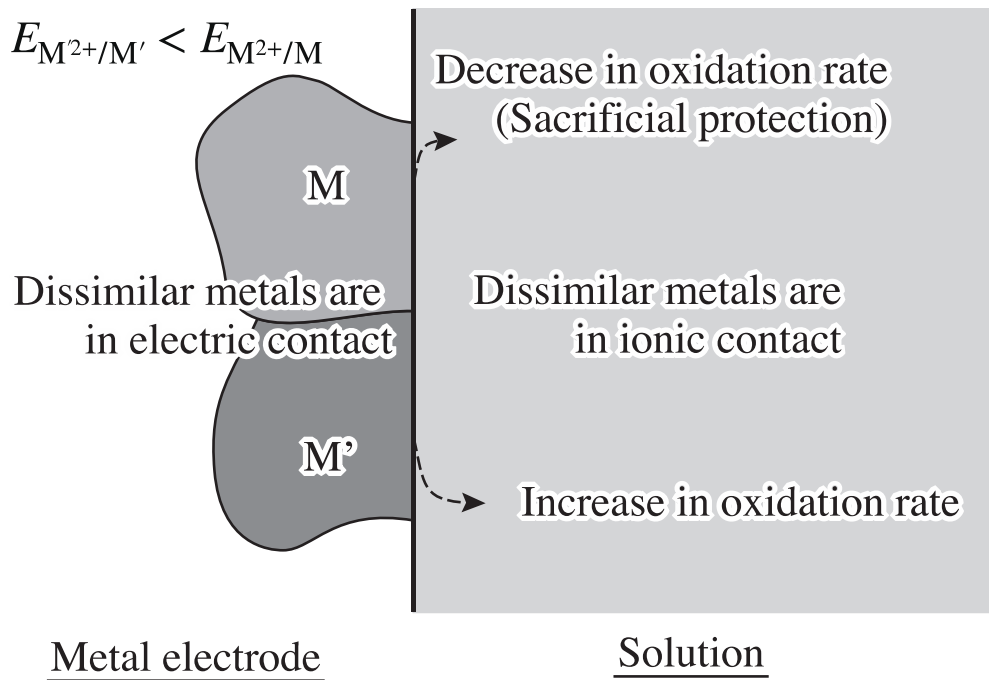


$E_{corr}$  is determined as the potential where the oxidation of M and the reduction of oxygen is balanced each other.

Since the current density of oxygen reduction reaches its maximum,  $i_{corr}$  is equal to that of oxygen reduction.

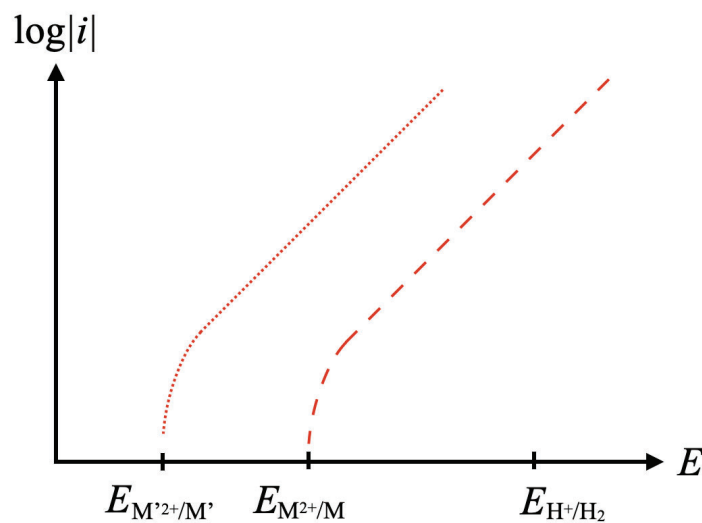
## Galvanic corrosion

What is galvanic corrosion?



## Galvanic corrosion

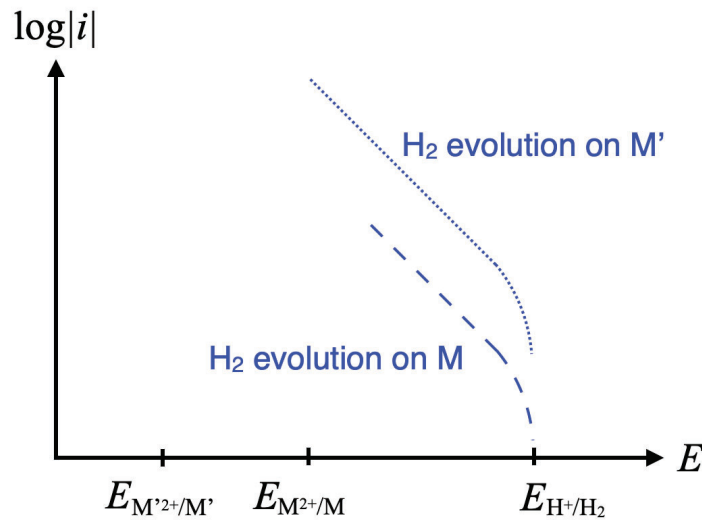
The oxidation reactions (dissolution) of M and M'



The oxidation of the metals occurs when the applied potential is more positive than the equilibrium potentials (Butler-Volmer equation).

## Galvanic corrosion

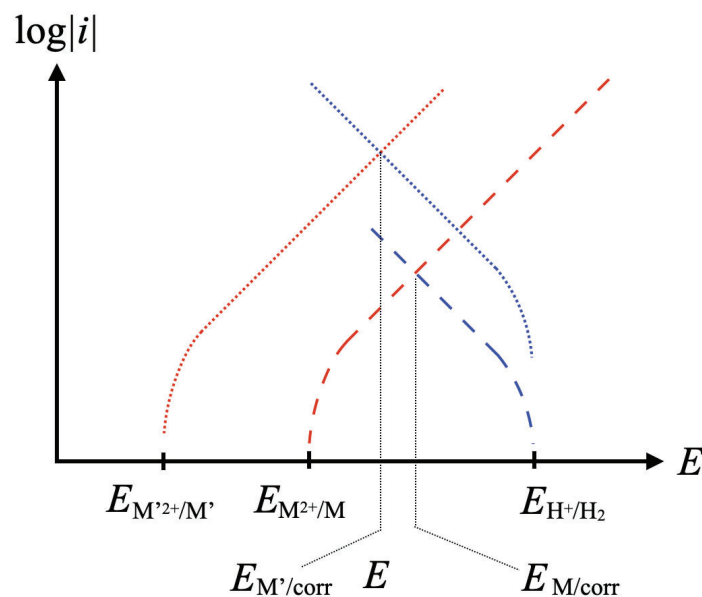
The reduction reactions ( $H_2$  evolution) on M and M'



Since the exchange current density for the  $H_2$  evolution depends on metal used as an electrode, two different curves are plotted from  $E_{H^+/H_2}$ .

## Galvanic corrosion

Corrosion potentials without electric contact

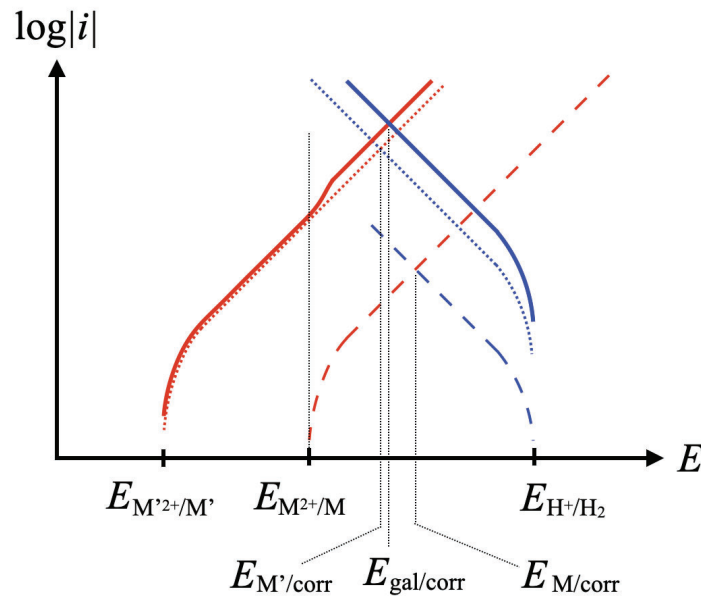


Without electric contact, the corrosion occurs on each metal even when M and M' are immersed in a common solution.



## Galvanic corrosion

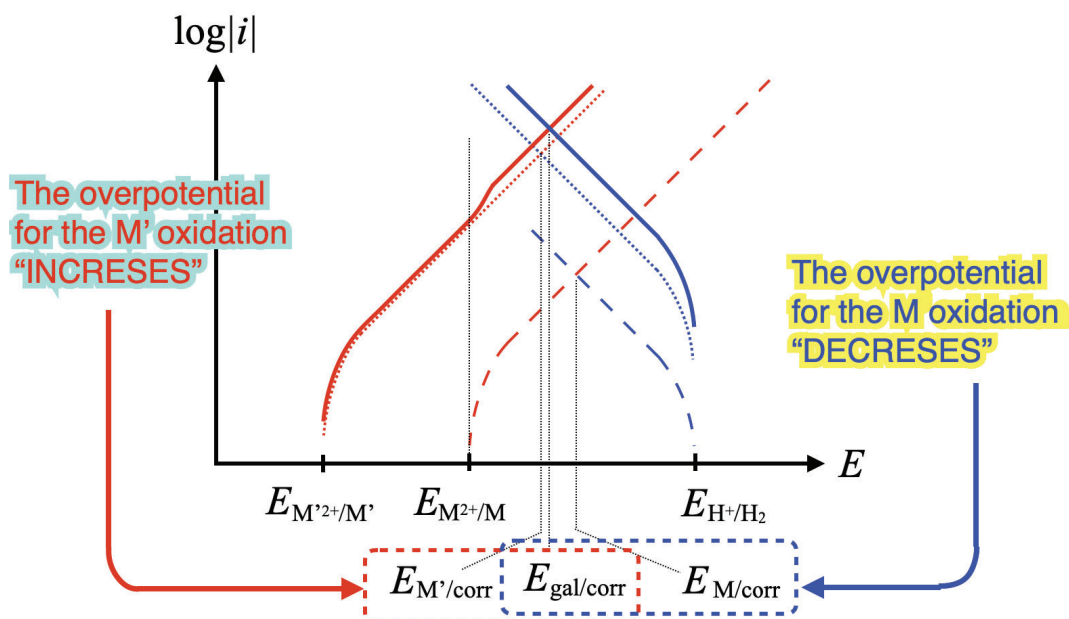
Corrosion potentials with both electric and ionic contact



The corrosion potential  $E_{gal/corr}$  is determined by both the total current density of oxidation and that of reduction.

## Galvanic corrosion

Sacrificial protection



The sacrificial protection of M is expected since the overpotential for the M oxidation decreases when M and M' in both electric and ionic contacts.

