# Lecture 28: Kinetics of Oxidation of Metals: *Part 1: rusting, corrosion, and the surface protection, all about chemistry*

Today's topics

- Chemical processes of oxidation of metals: the role played by oxygen.
- How to inhibit the oxidation depends on how effectively break up the contact between oxygen and the metals: the ways of anti-rusting and anti-corrosion.
- The kinetics of oxidation over the surface layer of metals can be described by the diffusion of metal cations (M^{n+}) and oxide anions (O^{2-}): diffusion flux as learned from Lecture 27.
- Understand how the Nernst potential forms between the outside and inner side of the metal oxide layer: solely caused by the difference in partial pressure of oxygen.

Basics of oxidation of metals:
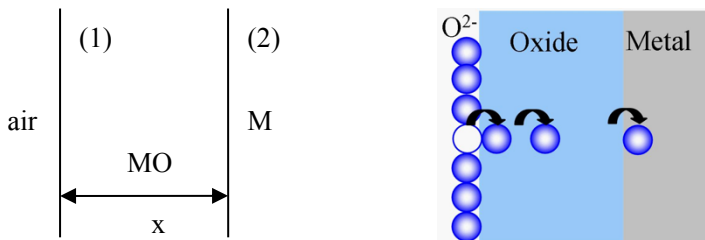
M: Metal; MO: metal oxide

- The initial stages of oxidation include oxygen adsorption and incorporation to the metal surface, oxide islands <u>nucleation</u>, and <u>growth</u> into a continuous film. Such a process represents a special case of phase transition that involves not just physical property change (as typical observed for most of the phase transformations we learned so far), but permanent chemical change of the components. Further oxidation requires the transport of either oxygen through the film to the metal/metal oxide interface, or that of the metal to the metal oxide/air interface. Thus, it is readily to see that the diffusion of metal and/or oxygen through the oxide film must somehow determine the kinetics of oxidation.
- The oxidation processes have been actively studied and are now understood relatively well. The kinetics of thick (>200 Å) oxide films approximately follows the <u>parabolic law</u>. It can be described, at least qualitatively, by the <u>Wagner model</u> of oxidation, in which *diffusion across the oxide film is the rate limiting process*. However, the situation is much more complicated in the case of very thin (<100 Å) films. The kinetic equations in this region cannot be integrated exactly, and only approximations for the oxide growth rate as a function of time can be obtained.
- Metal oxidation processes are extensively used in technology for protection of materials against rusting and corrosion, for which two major protection ways are mentioned here, for example, 1) **protective coatings:**

e.g., plating, painting, and cladding, providing a barrier of corrosion-resistant material between the air or water (containing oxygen) and the metal surface --- preventing the surface contact with oxygen. 2) **corrosion inhibitors**: one such example is acting as oxygen scavenger, for example *hydrazine* is a strong reducing agent, it is used as an *oxygen scavenger* to prevent corrosion in boiler water and hot-water heating systems.

Note: The bonding in most oxides is ionic, although some oxides do exhibit partially covalent bonding. For simplicity, let's assume ionic bonding for the metal oxide we will treat below. ***Thus, it is imperative that the diffusing species are electrically charged, i.e., M^{+2} and/or O^{-2}, rather than the neutral atoms of metal or molecules of oxygen.***
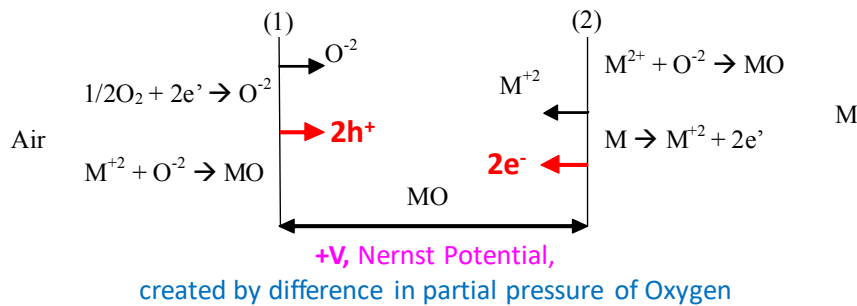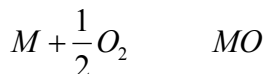

Where h^+ stands for hole, positive charge.

At the MO/air interface, the chemical potential of oxygen is given by

$$\mu_{O_2}^{(1)} = \mu_{O_2}^{0} + RT \ln p_{O_2}^{(1)}$$

where $p_{O_2}^{(1)}$ is the oxygen partial pressure in air.

At the M/MO interface, the equilibrium M/MO is established, so,

$$M + \frac{1}{2}O_2 \qquad MO$$

Then, $\mu_M + \frac{1}{2}\mu_{O_2}^{(2)} = \mu_{MO}$

Assuming M and MO to be pure (i.e., concentration is constant, and defined as unit), we have

$$\mu_M = \mu_M^0 + RT \ln C_M = \mu_M^0$$

$$\mu_{MO} = \mu_{MO}^0 + RT \ln C_{MO} = \mu_{MO}^0$$

Also, $\mu_{O_2}^{(2)} = \mu_{O_2}^{0} + RT \ln p_{O_2}^{(2)}$ where $p_{O_2}^{(2)}$ is the oxygen partial pressure at the M/MO interface.

Then, $\mu_M + \frac{1}{2}\mu_{O_2}^{(2)} = \mu_{MO} \rightarrow \mu_M^{0} + \frac{1}{2}\mu_{O_2}^{0} + \frac{1}{2}RT \ln p_{O_2}^{(2)} = \mu_{MO}^{0}$

Or, $\dfrac{1}{2}RT\ln p_{O_2}{}^{(2)} = \mu_{MO}{}^0 - \mu_M{}^0 - \dfrac{1}{2}\mu_{O_2}{}^0 = \Delta G^0 (<0)$

Or, $p_{O_2}{}^{(2)} = \exp[\dfrac{2\Delta G^0}{RT}]$

As $p_{O_2}{}^{(2)} < p_{O_2}{}^{(1)}$, the chemical potential of oxygen at the M/MO interface, $\mu_{O_2}{}^{(2)}$, is lower than that at the

MO/air interface, $\mu_{O_2}{}^{(1)}$. That is, $\mu_{O_2}{}^{(2)} < \mu_{O_2}{}^{(1)}$.

Also, $\mu_M{}^{(2)} = \mu_M{}^0 > \mu_M{}^{(1)} = \mu_M{}^0 + RT\ln C_M{}^{(1)}$, where $C_M{}^{(1)} << 1$

Thus, oxygen transport is favored from air/MO interface to M/MO interface, and metal transport is favored form M/MO interface to air/MO interface. *Since the bonding of MO is ionic, transport of M and O must occur as M^{+2} and O^{-2}, as depicted in the diagram above.*

We can see that there is a gradient in p_{O_2} across the oxide film, where at the air/MO interface $P_{O_2}{}^{(1)} \approx 0.21\,\text{atm}$

(with air as the atmosphere), and at the M/MO interface $P_{O_2}{}^{(2)} << 1$ atm. This creates a "so-called" Nernst

potential across the film given by $V = \dfrac{RT}{4F}\ln\{\dfrac{P_{O_2}{}^{(1)}}{P_{O_2}{}^{(2)}}\}$. This potential (with the air/MO side more positive)

represents a chemical equilibrium established by the reverse diffusion of M^{2+} and O^{2-} as depicted in the diagram above.

Transport of charged species occurs down an electrochemical potential gradient ($\dfrac{d\eta}{dx}$). Then we have the

diffusion flux for the two ions (Fick's first Law), as we learned from Lectures 5 and 26,

$J_{M^{+2}} = -C_{M^{+2}} \cdot \dfrac{D_{M^{+2}}}{k_B T} \cdot \dfrac{d\eta_{M^{+2}}}{dx}$ (in unit per atom), or $J_{M^{+2}} = -C_{M^{+2}} \cdot \dfrac{D_{M^{+2}}}{RT} \cdot \dfrac{d\eta_{M^{+2}}}{dx}$ (per mole)

$J_{O^{-2}} = -C_{O^{-2}} \cdot \dfrac{D_{O^{-2}}}{k_B T} \cdot \dfrac{d\eta_{O^{-2}}}{dx}$ (in unit per atom), or $J_{O^{-2}} = -C_{O^{-2}} \cdot \dfrac{D_{O^{-2}}}{RT} \cdot \dfrac{d\eta_{O^{-2}}}{dx}$ (per mole)

concentration   mobility

where $\eta's$ are the electrochemical potentials of the ions as defined below:

$\eta_{M^{+2}} = \mu_{M^{+2}} + ZF\Phi = \mu_{M^{+2}} + 2F\Phi$ (per mole) --- as we learned in Lecture 26

Where Φ — electrostatic potential, Z is the valence, F is Faraday constant = 96487 coulombs/mole = e $N_0 = 1.6\times10^{-19} \times 6.0\times10^{23}$

Similarly, $\eta_{O^{-2}} = \mu_{O^{-2}} - 2F\Phi$ (valence of O^{-2} is -2)

Note: the concentration of M^{+2} and O^{-2} are uniform, constant throughout the oxide film. Thus, we have

$$\frac{d\mu_{M^{+2}}}{dx} \approx 0 \quad ; \qquad \frac{d\mu_{O^{-2}}}{dx} \approx 0$$

$$\frac{d\eta_{M^{+2}}}{dx} = \frac{d\mu_{M^{+2}}}{dx} + 2F \cdot \frac{d\Phi}{dx} = 2F \cdot \frac{d\Phi}{dx}$$

Similarly, $\dfrac{d\eta_{O^{-2}}}{dx} = -2F \cdot \dfrac{d\Phi}{dx}$

Now by substituting the electrochemical potential gradient ($\dfrac{d\eta}{dx}$) back to the diffusion flux for the two ions as listed above:

We have, $\qquad\qquad J_{M^{+2}} = -\dfrac{C_{M^{+2}} \cdot D_{M^{+2}}}{RT} \cdot 2F \cdot \dfrac{d\Phi}{dx}$ (per mole)

$$J_{O^{-2}} = +\frac{C_{O^{-2}} \cdot D_{O^{-2}}}{RT} \cdot 2F \cdot \frac{d\Phi}{dx} \qquad \text{(per mole)}$$

Since the species are charged, when they transport, there must be electric current generated by each of the ions as defined below:

$$I_{M^{+2}} = 2e \cdot J_{M^{+2}} \quad ; \qquad I_{O^{-2}} = -2e \cdot J_{O^{-2}}$$

Where, e = electronic charge = F/N_0, N_0 is the Avogadro's constant, 6.02×10^{23} #/mole.

So, $\qquad\qquad I_{M^{+2}} = -\dfrac{C_{M^{+2}} D_{M^{+2}} 4F^2}{RTN_0} \cdot \dfrac{d\Phi}{dx}$ (ampere /cm^2)

$$I_{O^{-2}} = -\frac{C_{O^{-2}} D_{O^{-2}} 4F^2}{RTN_0} \cdot \frac{d\Phi}{dx}$$

Now, oxygen ions (O^{-2}) move from MO/air interface[1] to M/MO interface[2], and M^{+2} move from (2) to (1). *Thus, both of the electrical currents due to the transport of ions are of the same sign.*

We know that, $E = -\dfrac{d\Phi}{dx} \rightarrow$ electric field, as also learned in Lectures 26 and 27.

Also, we have

$$\sigma_{M^{+2}} = \frac{4F^2}{RTN_0} \cdot C_{M^{+2}} D_{M^{+2}}; \quad \sigma_{O^{-2}} = \frac{4F^2}{RTN_0} \cdot C_{O^{-2}} D_{O^{-2}} \quad \text{defined as } \textbf{ionic conductivities } (\text{ohm}^{-1}.\text{cm}^{-1}).$$

Thus, $\quad I_{M^{+2}} = \sigma_{M^{+2}} E; \quad$ and $\quad I_{O^{-2}} = \sigma_{O^{-2}} E$

The total ionic current density caused by the diffusion of both ions is:

$$I_{ion} = I_{M^{+2}} + I_{O^{-2}}$$

$$= (\sigma_{M^{+2}} + \sigma_{O^{-2}}) \cdot E$$

$$= \sigma_{ion} E = -\sigma_{ion} \frac{d\Phi}{dx}$$

Assuming if only ionic current flows through the oxide film, the transport will quickly stop as soon as enough M^{+2} ions are transported to MO/air interface, and/or enough O^{-2} ions are transported to M/MO interface to

reach the equilibrium as defined by the Nernst Potential $V = \dfrac{RT}{4F} \ln\{\dfrac{P_{O_2}^{(1)}}{P_{O_2}^{(2)}}\}$ as mentioned above. However,

that the oxide film also conducts electrons and/or electron holes, and flow of these electrons and holes neutralize the flow of the M^{2+} and O^{2-} ions --- the overall result combining these two pairs of diffusion is that O_2 moves to the M/MO interface and M moves to the air/MO interface, to keep the oxide layer growing and maintain the Nernst Potential (i.e., the *thermodynamic driving force* for the phase growth) until the oxide layer becomes too thick, i.e., the diffusion across the whole layer takes 'forever' (now becoming *Kinetics limited*). --- details to be continued in next Lecture.