Lecture 29: Kinetics of Oxidation of Metals: *Part 2: Wagner Parabolic Model*

Today's topics

- Oxidation of metals: controlled by both the ionic diffusion (carried by M^{+2} and O^{-2}) and the electronic diffusion (carried by e^- and h^+).
- Combination of the ionic diffusion and electronic diffusion gives a net result of diffusion that apparently shows the diffusion of molecular oxygen (O_2) from the air/MO interface to the MO/M interface, and the reverse for the diffusion of metal atoms. This way maintains the Nernst potential caused by the difference of partial pressure of oxygen at the two interfaces.
- Understanding of the Wagner's parabolic model that describes the rate of growth of the MO layer: implications for how to inhibit the growth of oxide for the purpose of protecting the metals from corrosion.

Last Lecture:

Since the metal oxide is of ionic lattice, the diffusion across the oxide layer (that controls the growth of the oxide phase) should be carried out by ions, M^{+2} and/or O^{-2}, rather than the neutral atoms of metal or molecules of oxygen, as depicted in the diagram below.
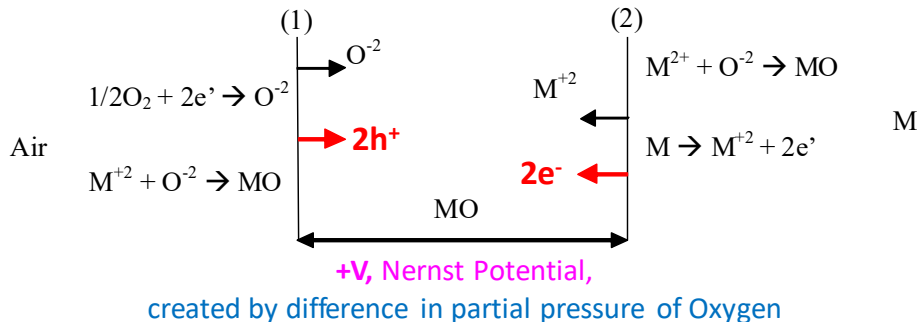
The total ionic current density caused by the diffusion of both ions is:

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

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

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

As can be seen from the diagram above, there is a gradient in p_{O_2} across the oxide film, where at the air/MO interface $P_{O_2}^{(1)} \approx 0.21$ 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.*

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*).

Today's Lecture:
Continue to discuss the diffusion flux involving the **electrons and holes, e⁻ and h⁺**. Combining this diffusion pair to the diffusion pair of M^{2+} and O^{2-} ions leads to the Wagner's parabolic rate law, which describes the kinetics (rate) of the MO layer growth.

The electronic current density is given by $I_{el} = -\sigma_{el} \cdot \dfrac{d\varphi}{dx} = -(\sigma_e + \sigma_h) \cdot \dfrac{d\varphi}{dx}$

Where $\sigma_e =$ electron conductivity

$\sigma_h =$ hole conductivity

$\sigma_{el} =$ total electronic conductivity

$\varphi =$ electrochemical potential of electrons divided by the electronic charge

Now, there is no externally applied voltage. Therefore, the net current through the film must be zero. That is

$I_{ion} + I_{el} = 0$

To preserve electroneutrality.

Thus, $\sigma_{ion} \dfrac{d\Phi}{dx} + \sigma_{el} \dfrac{d\varphi}{dx} = 0$

The overall process can be schematically described as the following schematics:

+V, Nernst Potential, created by difference in partial pressure of Oxygen
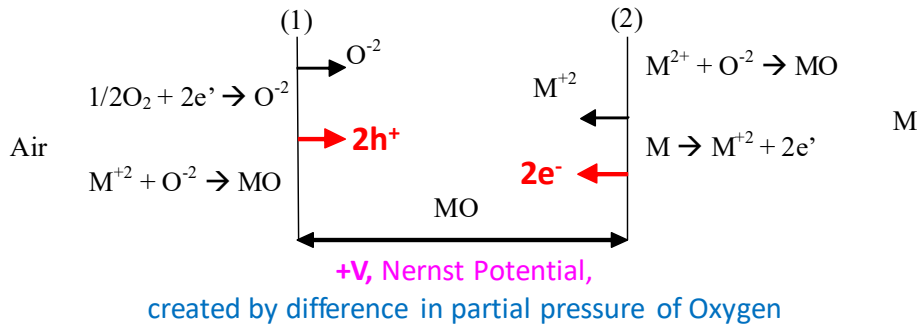
The above figure shows that for every one O^{-2} ion moving, **2h$^+$** move in the same direction; and for every one M^{+2} moving, **2e$^-$** move in the same direction.

The net result is that there is no net current. However, there is the so-called internal current. The above can be represented by an equivalent circuit:
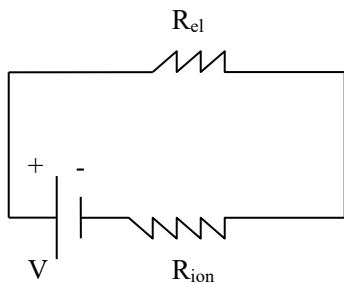
The internal current density, $I_{int} = \dfrac{V}{R_{ion} + R_{el}}$, where V is the Nernst potential

R_{ion} = Ionic resistance per unit area $= x / \sigma_{ion}$, where x is the thickness of metal oxide.

R_{el} = electronic resistance per unit area $= x / \sigma_{el}$

Then,

$$I_{int} = \frac{V}{\dfrac{x}{\sigma_{ion}} + \dfrac{x}{\sigma_{el}}} = \frac{V \sigma_{ion} \sigma_{el}}{(\sigma_{ion} + \sigma_{el})} \cdot \frac{1}{x} \qquad (1)$$

Also we have, $\quad I_{int} = \dfrac{dQ}{dt} \qquad (2)$

Where, dQ = charge (internal) transported in time 'dt'

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When "dQ/unit area" ionic charge is passed through the film (and of course an equal amount of electronic charge also passed through), the "molar number of MO/unit area" to be formed can be written as:

$$dn = \frac{dQ}{2F}$$

where **F:** Faraday constant, $= 96487$ coulombs/mole $= e\, N_0 = 1.6 \times 10^{-19} \times 6.0 \times 10^{23}$ (see Lecture 29)

If W_{MO} is the molecular weight of MO, then

$$W_{MO}dn = \frac{dQ}{2F}W_{MO} \quad \text{(with unit of gram/unit area, e.g., cm}^2\text{)}$$

If ρ_{MO} is the density of MO, then

$$\frac{W_{MO}}{\rho_{MO}}dn = \frac{W_{MO}}{\rho_{MO}} \cdot \frac{dQ}{2F}, \quad \text{is the volume of MO formed (created) per unit area}$$

Since volume = unit area (1.0) × dx (change in thickness) = dx

So, $$\frac{W_{MO}}{\rho_{MO}} \cdot \frac{dQ}{2F} = dx$$

Or, $$dQ = \frac{2F\rho_{MO}}{W_{MO}} \cdot dx \qquad (3)$$

Substituting Eq. (3) into Eq. (2), we have

$$I_{int} = \frac{dQ}{dt} = \frac{2F\rho_{MO}}{W_{MO}} \cdot \frac{dx}{dt} \qquad (4)$$

Comparing Eq. (4) and Eq. (1), we have

$$I_{int} = \frac{2F\rho_{MO}}{W_{MO}} \cdot \frac{dx}{dt} = \frac{V\sigma_{ion}\sigma_{el}}{(\sigma_{ion}+\sigma_{el})} \cdot \frac{1}{x}$$

then, $$xdx = \frac{W_{MO}\sigma_{ion}\sigma_{el}V}{2F\rho_{MO}(\sigma_{ion}+\sigma_{el})} \cdot dt$$

Integration of the above equation gives:

$$x^2 = \frac{W_{MO}\sigma_{ion}\sigma_{el}V}{F\rho_{MO}(\sigma_{ion}+\sigma_{el})} \cdot t \qquad\qquad (5)$$

Eq. (5) can be re-written in the format of

$$x^2 = Kt \qquad\qquad (6)$$

Where, $K = \dfrac{W_{MO}}{F\rho_{MO}} \cdot \dfrac{\sigma_{ion}\sigma_{el}V}{(\sigma_{ion}+\sigma_{el})}$, is the ***oxidation rate constant***, in unit of length²/second, e.g., cm²/sec.

Eq. (6) is known as the *Wagner's parabolic rate law, or Wagner's parabolic model.*

The rate constant, K, contains both the thermodynamic and the kinetic factors.

- The thermodynamic factor is embodied in the Nernst potential **'V'**, which is related to the free energy for the reaction:

$$M + \frac{1}{2}O_2 \underset{\longleftarrow}{\longrightarrow} MO$$
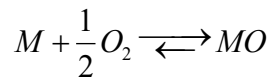
- The kinetic factor is embodied in the term

$$\frac{\sigma_{ion}\sigma_{el}}{\sigma_{ion}+\sigma_{el}}$$

Note that if either $\sigma_{ion} \to 0$ or $\sigma_{el} \to 0$, the kinetics of oxidation will be very slow.

- If $\sigma_{ion} \gg \sigma_{el}$, then the rate constant is

$$K \approx \frac{W_{MO}}{F\rho_{MO}} \cdot \sigma_{el}V$$

- If $\sigma_{el} \gg \sigma_{ion}$, then

$$K \approx \frac{W_{MO}}{F\rho_{MO}} \cdot \sigma_{ion}V$$

Supposing the latter situation ($\sigma_{el} \gg \sigma_{ion}$) describes the kinetics of oxidation, since

$$\sigma_{ion} = \sigma_{M^{+2}} + \sigma_{O^{-2}}$$

Then, the larger of the two will dictate the kinetics.

Supposing $\sigma_{M^{+2}} \gg \sigma_{O^{-2}}$, then, the rate constant is $K \approx \dfrac{W_{MO}}{F\rho_{MO}} \cdot \sigma_{M^{+2}} V$

Since $\qquad \sigma_{M^{+2}} = \dfrac{4F^2}{RTN_0} \cdot C_{M^{+2}} \cdot D_{M^{+2}}$, where N_0 is the Avagadro constant.

Then: $\qquad K \approx \dfrac{4FW_{MO}}{RTN_0\rho_{MO}} \cdot C_{M^{+2}} \cdot D_{M^{+2}} V$

The suppression of the kinetics of oxidation of metals and alloys thus would require that the diffusion coefficient of M^{+2} in the oxide be suppressed to prevent the oxidation of a given metal or alloy.

Some following up remarks about oxidation of metals:

1. Transport properties of oxides, halides, sulfides, carbonates, etc, can be changed by doping with ions of a valence different from the host ion — the so-called aliovalent dopant ('alio' means different). This is similar to case of semiconductor materials wherein the concentrations of electrons and holes are altered by introducing aliovalent dopants.
2. The general theory of oxidation of metals is equally applicable to halides, sulfides, sulfates, carbonates, nitrates, etc..
3. Most super alloys based on Fe, Ni, and Co contain other elements to improve the oxidation resistance.

   For example, many of the alloys contain Al or Cr. The partial pressure (required P_{O_2}) for the oxidation of Al to Al_2O_3 and Cr to Cr_2O_3 is much lower than for Fe to FeO (Fe_2O_3), Ni to NiO and Co to CoO. The oxidation resistance of the super-alloys is enhanced by the formation of a protective layer of Al_2O_3 or Cr_2O_3 on the surface.