금속 소재의 환경노출거동: 14주차

Degradation Behavior of Metals and Alloys

after Exposure to Elements: 14th Lecture

날짜: 2020년 12월 4일

■ Butler-Volmer 식의 유도 계속
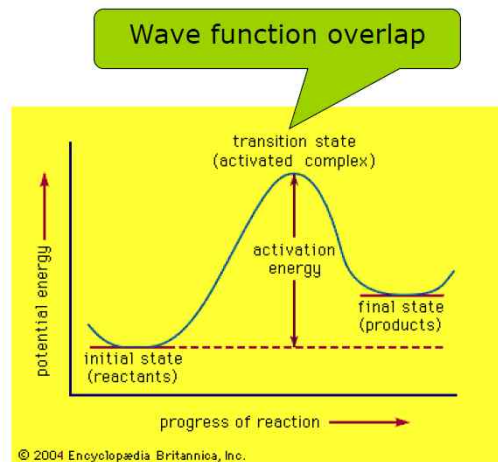
● Arrhenius-type equation을 전기 화학 반응에도 적용시킴.

Arrhenius Equation

$$k = Ae^{-\left(E_A/RT\right)}$$
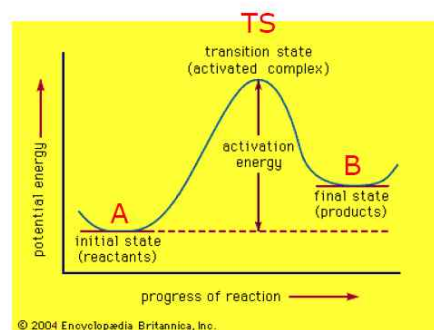
$$k = A'e^{-\left(\Delta G^{\neq}/RT\right)}$$
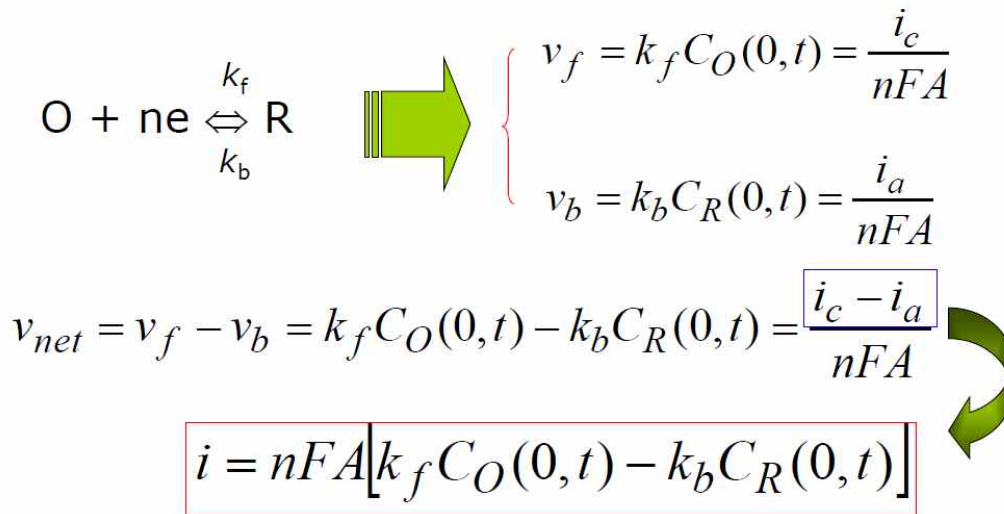

Wave function overlap

Transition-State Theory

▫ At equilibrium

- $k_f C_A = f_{AB}k'C_{TS}$; $k_b C_B = f_{BA}k'C_{TS}$
- $f_{AB} = f_{AB} = \kappa/2$

$$k_f = \frac{\kappa}{2}k'e^{-\left(\Delta G_f^{\neq}/RT\right)}$$

$$k_b = \frac{\kappa}{2}k'e^{-\left(\Delta G_b^{\neq}/RT\right)}$$

● Arrhenius-type equation을 전기 화학 반응에도 적용시킴.

Electrode Reactions

$$O + ne \Leftrightarrow R \quad \overset{k_f}{\underset{k_b}{}}$$

$$v_f = k_f C_O(0,t) = \frac{i_c}{nFA}$$

$$v_b = k_b C_R(0,t) = \frac{i_a}{nFA}$$

$$v_{net} = v_f - v_b = k_f C_O(0,t) - k_b C_R(0,t) = \frac{i_c - i_a}{nFA}$$

$$i = nFA[k_f C_O(0,t) - k_b C_R(0,t)]$$

Butler – Volmer Equation

John Alfred Valentine Butler

□ John Alfred Valentine Butler (born 14 February, 1899) was the British physical chemist who was the first to connect the kinetic electrochemistry built up in the second half of the twentieth century with the thermodynamic electrochemistry that dominated the first half. He had to his credit, not only the first exponential relation between current and potential (1924), but also (along with R.W. Gurney) the introduction of energy-level thinking into electrochemistry (1951).

□ However, Butler did not get all quite right and therefore it is necessary to give credit also to Max Volmer, a great German surface chemist of the 1930 and his student Erdey-Gruz. Butler's very early contribution in 1924 and the Erdey-Gruz and Volmer contribution in 1930 form the basis of phenomenological kinetic electrochemistry. The resulting famous Butler-Volmer equation is very important in electrochemistry.

□ Butler was the quintessential absent-minded research scientist of legend, often lost to the world in thought. During such periods of contemplation he sometimes whistled softly to himself, though he was known on occasion to petulantly instruct nearby colleagues to be quiet.

● p. 2 맨 위의 과전압 vs. 전류 밀도 좌표계의 직선의 방정식을 유도하려면 Tafel equation을 유도해야 하는데 이는 먼저 Butler-Volmer식을 유도해야 함.
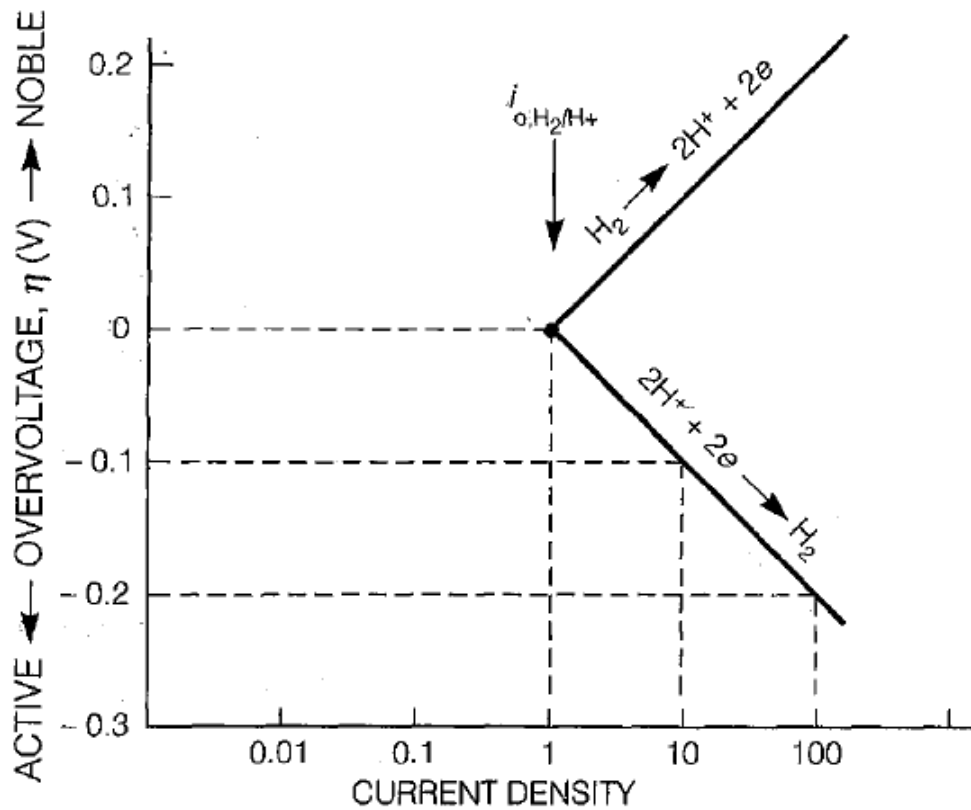
Activation overpotential showing Tafel behavior.

● 다음의 내용을 동영상 강의에서 상세히 설명하였음.

$$\Delta G_f{}^* - \Delta G_r{}^* = \Delta G_{H^+/H_2} = -nFe_{H^+/H_2}.$$

The Maxwell distribution law gives the energy distribution of reacting species and leads to expressions for forward, r_f, and reverse, r_r, reaction rates as a function of the respective activiation energies:

$$r_f = K_f \exp\left[-\frac{\Delta G_f{}^*}{RT}\right]$$

and

$$r_f = K_f \exp\left[-\frac{\Delta G_r{}^*}{RT}\right]$$

where K_f and K_r are the reaction rate constants for the forward and reverse reactions, respectively. At equilibrium,

$$r_f = r_r = \frac{i_o a}{nF}, \tag{7}$$

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Thus

$$i_o = K_f' \exp(-\Delta G_f^*/RT) = K_r' \exp(-\Delta G_r^*/RT),$$

which clearly demonstrates that exchange current density is a function of the activation energies.

● Butler-Volmer 방정식의 유도에 수반하는 기본적 가정은 p. 1에 기술한 Transition-State Theory (Activated Complex Theory)의 전기 화학 반응, 특별히 다음의 정반응과 역반응에 대해서 응용할 수 있다는 것이다.
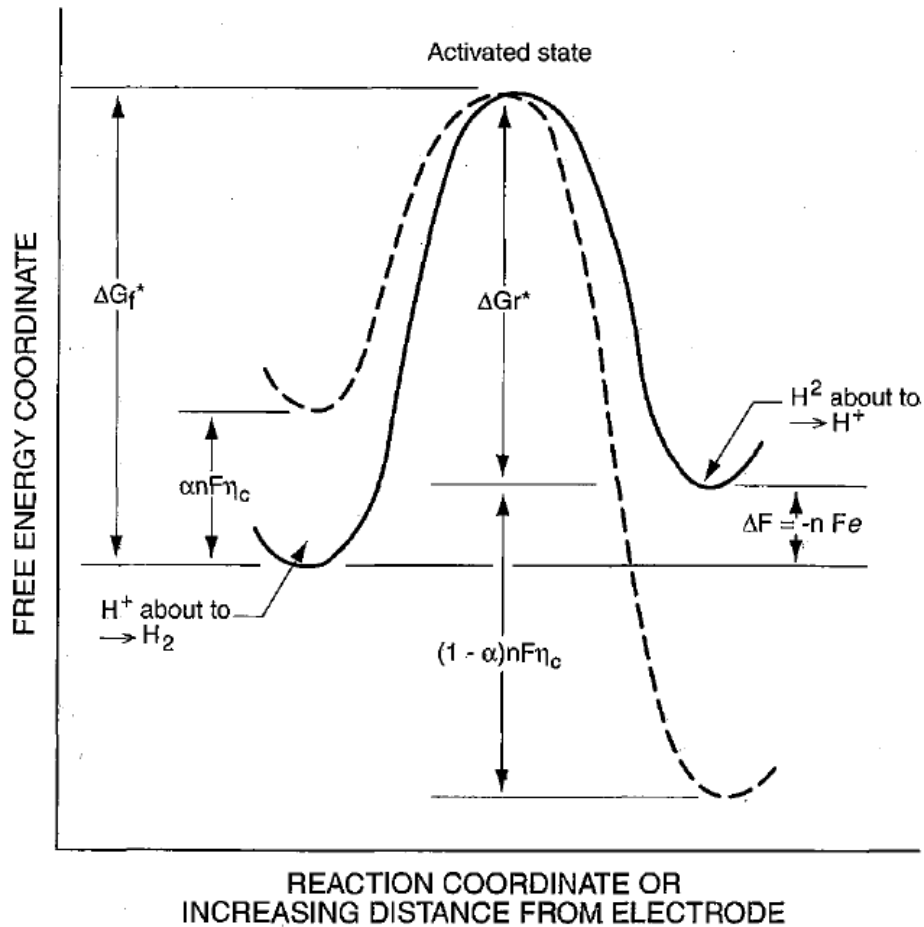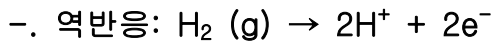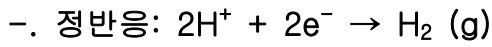
-. 정반응: $2H^+ + 2e^- \rightarrow H_2$ (g)

-. 역반응: H_2 (g) $\rightarrow 2H^+ + 2e^-$

FIGURE 3.3   Activation energy model for activation overpotential. Equilibrium state (————); polarized state (———)

When a cathodic overpotential, η_c, is applied to the electrode, the discharge reaction rate is reduced and that of the ionization is increased. This is accomplished by decreasing the activation energy for the discharge reaction by an amount, $\alpha nF\eta_c$, and increasing that for the ionization reaction by an amount, $(1-\alpha)nF\eta_c$, as indicated by the dashed line in Figure 3.3. The factors α and $(1-\alpha)$ are the fractions of η_c taken by the discharge and ionization (forward and reverse) reactions, respectively. The cathodic discharge reaction rate in terms of current density becomes

$$i_c = K_f' \exp\left[-\frac{\Delta G_f{}^* - \alpha nF\eta_c}{RT}\right],$$

and the anodic ionization reaction rate becomes

$$i_a = K_r' \exp\left[-\frac{\Delta G_f{}^* + (1-\alpha)nF\eta_c}{RT}\right].$$
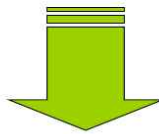
The net applied current is then

$$i_{app,c} = i_c - i_a = i_o \exp\left[\frac{\alpha nF\eta_c}{RT}\right] - i_o \exp\left[\frac{-(1-\alpha)nF\eta_c}{RT}\right], \qquad (11)$$

For an applied anodic current favoring ionization to H^+,

$$i_{app,a} = i_a - i_c = i_o \exp\left[\frac{\alpha nF\eta_a}{RT}\right] - i_o \exp\left[\frac{-(1-\alpha)nF\eta_a}{RT}\right], \qquad (12)$$

Butler-Volmer Formulation

$$k_b = k^o e^{(1-\alpha)\frac{nF}{RT}\left(E-E^{o'}\right)} \qquad k_f = k^o e^{-\alpha\frac{nF}{RT}\left(E-E^{o'}\right)}$$

$$i = nFAk^o\left[C_O(0,t)e^{-\alpha\frac{nF}{RT}\left(E-E^{o'}\right)} - C_R(0,t)e^{(1-\alpha)\frac{nF}{RT}\left(E-E^{o'}\right)}\right]$$

Cathodic current   Anodic current

applied to any electrochemical reactions under any conditions

Max Volmer

- Max Volmer (3 May 1885 in Hilden – 3 June 1965 in Potsdam) was a German physical chemist, who made important contributions in electrochemistry, in particular on electrode kinetics. He co-developed the Butler-Volmer equation.
- Volmer held the chair and directorship of the Physical Chemistry and Electrochemistry Institute of the Technische Hochschule Berlin, in Berlin-Charlottenburg. After World War II, he went to the Soviet Union, where he headed a design bureau for the production of heavy water. Upon his return to East Germany ten years later, he became a professor at the Humboldt University of Berlin and was president of the East German Academy of Sciences.

Butler-Volmer Model

electrode potential only changes the electron energy

reduction ← — oxidation →

Na(Hg)   Na$^+$ + e

reduction ← — oxidation →

Na(Hg)

Potential more positive

Na$^+$ + e

Potential more negative

reduction ← — oxidation →

Na$^+$ + e

Na(Hg)