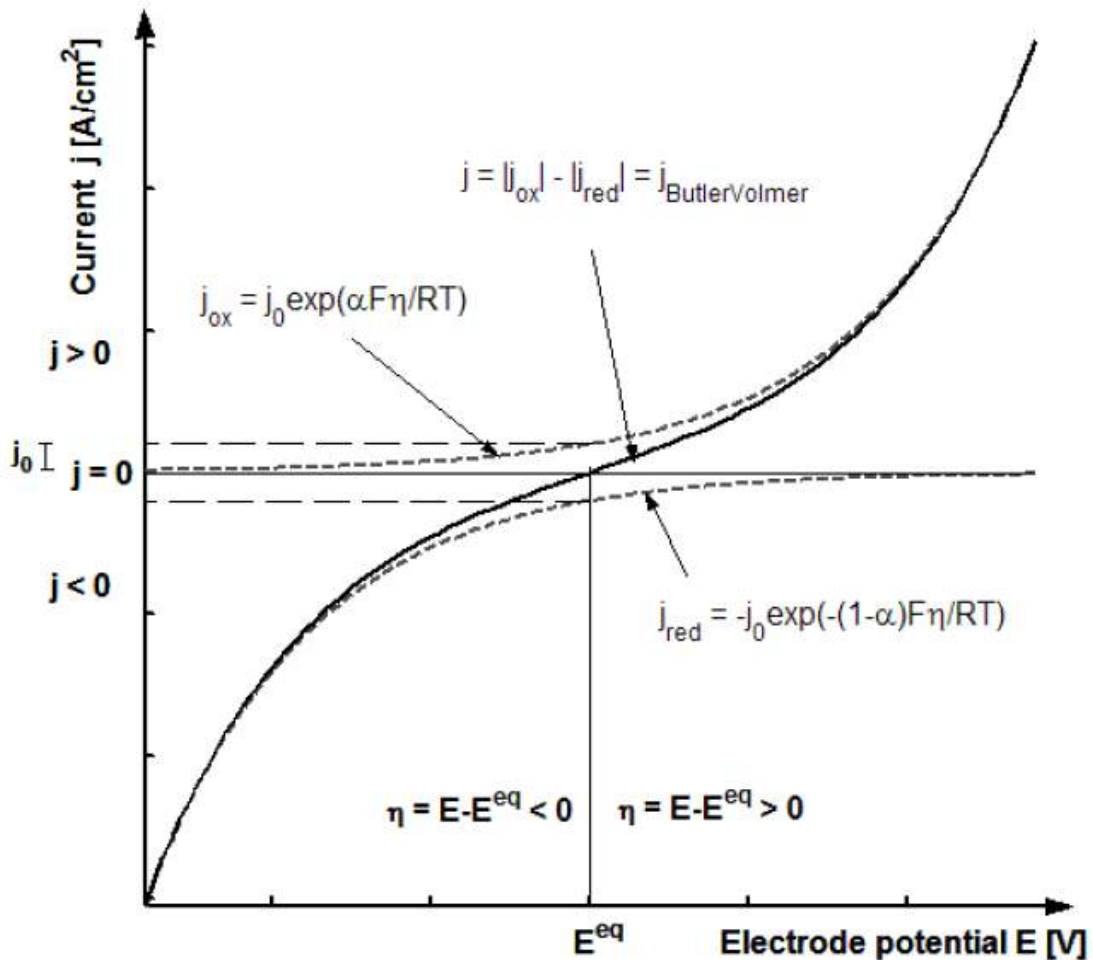


금속 소재의 환경노출거동: 15주차
 Degradation Behavior of Metals and Alloys
 after Exposure to Elements: 15th Lecture

날짜: 2020년 12월 11일

■ Butler-Volmer 식으로부터 Tafel equation의 유도

● Butler-Volmer식의 수학적 형태와 도해 (graphical forms) → 강의 동영상에서 설명한 내용을 그림으로 나타내었음.



● 이제 과전압이 평형 전위로부터 얼마나 변하는가에 따라 Butler-Volmer식이 수학적으로 또한 형상이 어떻게 변할까? →

세 가지 경우의 수를 고려 함. Simplification of Butler-Volmer Equation

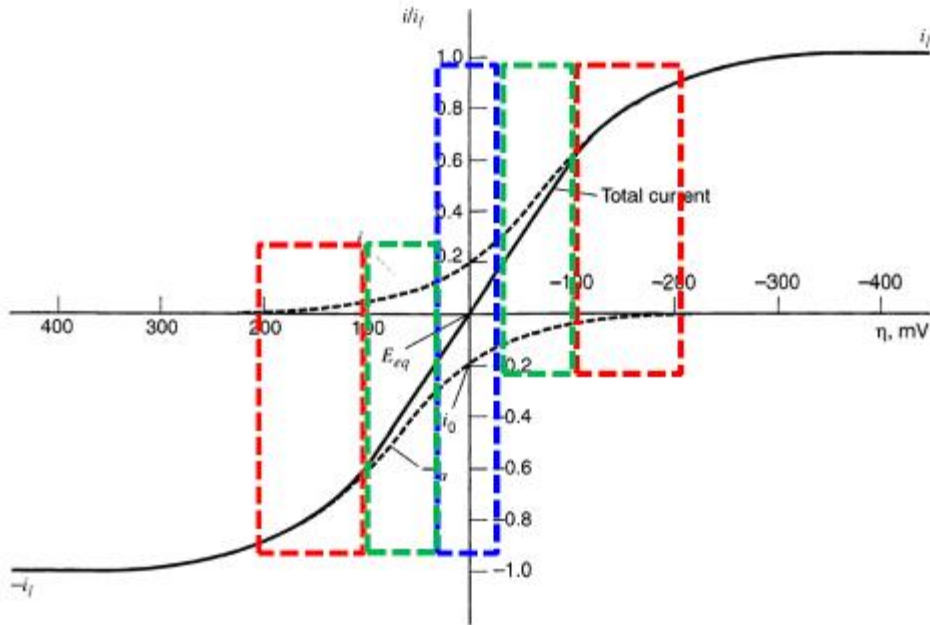


Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a .

1. 위 그림에서 파란색 점선으로 표시된 구역임 → Reversible Reaction at Very Small Overpotential

- Maclaurin 급수 전개에 의한 linear polarization 관계식을 얻음

- At a very small overpotential ($|\eta| < 10$ mV), the exponents in the equation are small enough to expand both of them taking into account that $e^x \approx 1 + x$:

$$j = j_o \left[\exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \exp \left\{ \frac{-\beta nF\eta}{RT} \right\} \right] = j_o \left[\left\{ 1 + \frac{(1 - \beta)nF\eta}{RT} \right\} - \left\{ 1 + \frac{-\beta nF\eta}{RT} \right\} \right]$$

$$j = \frac{j_o n F \eta}{RT}$$

in which the current density is proportional to overpotential.

→ 전류 밀도가 과전압에 비례하는 1차 함수 꼴을 얻음.

2. 과전압이 아주 큰 Tafel region (p. 2의 그림에서 빨간 색 점 선으로 표시된 구간 임.)

(1) Anodic Overpotential이 아주 큰 경우

$$j = j_o \left[\exp \left\{ \frac{(1 - \beta)nF\eta}{RT} \right\} - \exp \left\{ \frac{-\beta nF\eta}{RT} \right\} \right] = j_o \left[\left\{ 1 + \frac{(1 - \beta)nF\eta}{RT} \right\} - \left\{ 1 + \frac{-\beta nF\eta}{RT} \right\} \right]$$

- When the electrode is highly anodically polarized, $\eta \gg 0$, the second term of the equation is very small and the equation is simplified to:

$$j = j_o \exp \left[\frac{(1 - \beta)nF\eta}{RT} \right]$$

- When $\eta \gg 0$ (large anodic polarization),

$$j = j_o \exp \left[\frac{(1 - \beta)nF\eta}{RT} \right] \eta = - \left[\frac{RT}{(1 - \beta)nF} \right] \ln j_o + \left[\frac{RT}{(1 - \beta)nF} \right] \ln j$$

(a)

위의 왼편의 식 양변에 자연 로그를 취하면 오른편과 같은 Tafel 방정식 (a)를 얻음.

(2) Cathodic Overpotential이 아주 큰 경우

- When $\eta \ll 0$ (large cathodic polarization), consider only absolute value

$$|j| = j_o \exp \left[\frac{-\beta nF\eta}{RT} \right] \quad \eta = \left[\frac{RT}{\beta nF} \right] \ln j_o - \left[\frac{RT}{\beta nF} \right] \ln |j|$$

(b)

전류 밀도의 절대값만 고려하고 위의 왼편의 식 양변에 자연 로그를 취하면 오른편과 같은 Tafel 방정식 (b)를 얻음.

-. 위의 식 (a)와 (b)를 도해하면 p. 4의 그림과 같은 함수 형태를 얻음. → 과전압이 양의 방향과 음의 방향으로 아주 큰 빨간 점선 구간임.

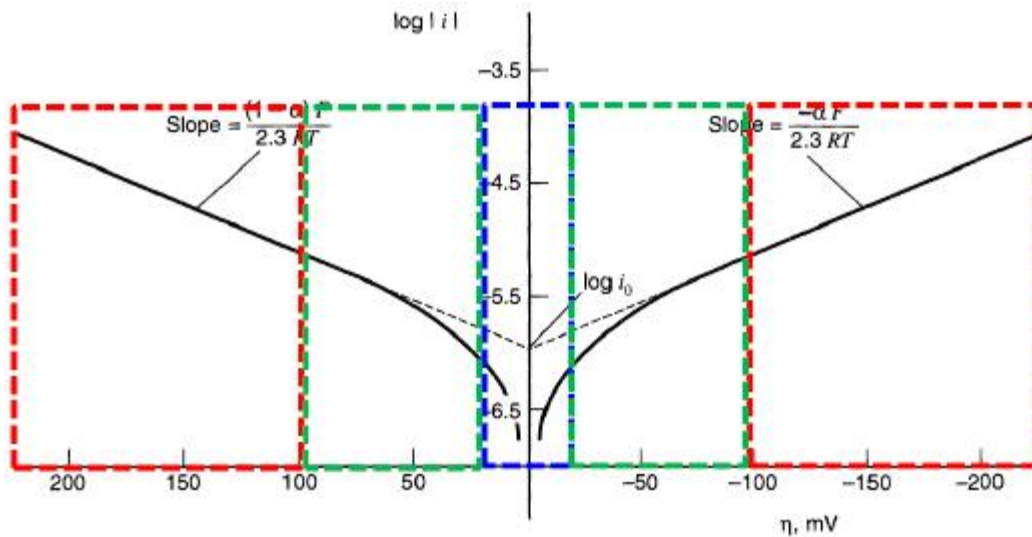


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

- A plot of $\log i$ vs. η

→ known as a **Tafel plot**

→ can obtain the values of α and i_0

→ At large negative overpotentials

$$\eta = \frac{2.3RT}{\alpha F} \log i_0 - \frac{2.3RT}{\alpha F} \log i$$

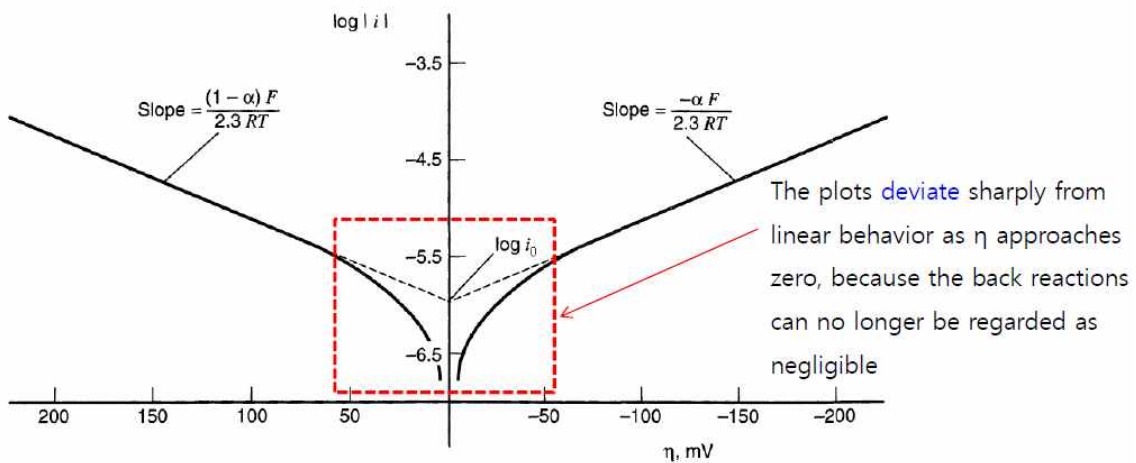


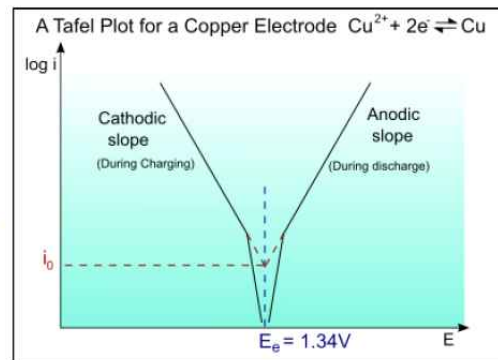
Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

- Tafel 방정식의 직선 구간의 의미는 역반응 속도를 무시할 수 있다는 가정 하에서 유도한 것임. 그러나 과전압의 크기가 아주 작아지면 빨간 점선 구간에 해당하는데 이때는 역반응의 속도도 무시할 수 없게 됨.

Tafel Plots

Slope: α
Intercept: i_0

- Very small η
 - $i = -i_0 F \eta / RT$ and $R_{CT} = |\eta / i| = RT / n F i_0$
- Very large η
 - Negative η , $i = i_0 e^{-\alpha n f \eta}$
 - Positive η , $i = i_0 e^{(1-\alpha) n f \eta}$
- From the plot, i_0 (k°) and α can be determined.



experimentally sometimes nonlinear profiles appear, suggesting multiple reactions

- 지금까지 설명했던 Tafel plot을 요약하면 위와 같음 → 기울기는 symmetry factor α , 절편은 교환 전류 밀도 i_0 임.

- 실험결과를 Tafel plot한 결과 비선형이 되는 경우는 전하 이동 반응이 여러개 임을 암시 함.

3. 결론

- 전기 화학 반응과 화학 반응의 가장 큰 차이는 화학 반응과 달리 전기 화학 반응의 경우, 특히 반응물의 농도가 아주 커서 반응물 고갈에 수반되는 물질 이동을 고려할 필요가 없는 경우, 전극 전위가 반응 활성화 에너지에 큰 영향을 줌 → 이를 반영한 결과가 Butler-Volmer 방정식 임. → p. 6 위의 자료 참조

Electrochemical and Chemical Reactions

- | | |
|--|--|
| <ul style="list-style-type: none"> □ Net Reaction Rate = difference between forward and backward reactions □ Transition State Theory <ul style="list-style-type: none"> ■ Arrhenius equation | <ul style="list-style-type: none"> □ Net Reaction Rate = difference between forward and backward reactions □ Transition State Theory <ul style="list-style-type: none"> ■ Arrhenius equation |
| <ul style="list-style-type: none"> □ Effects of Electrode Potential on Reaction Activation Energy <ul style="list-style-type: none"> ■ Extent of influence varies between the cathodic and anodic processes (α) ■ Butler-Volmer equation | <ul style="list-style-type: none"> □ Independence of Potential |

- . 본 강의록 동영상에서는 다음의 수학적 형태를 이용하였으나 궁극적으로 Butler-Volmer 방정식과 Tafel plot의 의미는 동일함. For an applied anodic current favoring ionization to H^+ ,

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

where α is now the fraction of η_a taken by the anodic ionization reaction. For high values of η_c , (11) simplifies to

$$i_{app,c} = i_c - i_o = i_o \exp\left[\frac{\alpha n F \eta_c}{RT}\right]$$

which is identical to

$$\eta_{act,c} = \beta_c \log \frac{i_c}{i_o} \quad (10b)$$

with $\beta_c = 2.3RT/\alpha n F$; and (12) becomes

$$\eta_{act,a} = \beta_a \log \frac{i_a}{i_o} \quad (10a)$$

for high values of η_a . For $\alpha = 0.5$, β_c or β_a is 0.12 V, near the assumed value of 0.1 V used for the approximate calculations in this book.



Julius Tafel

The year 1898 marked a turning point in organic electrochemistry with Swiss chemist **Julius Tafel** (1862-1918) demonstrating the use of lead as an electrode for the reduction of organic compounds. Tafel, who was both an organic chemist and a physical chemist, made seminal contributions to organic electrochemistry and established the Tafel equation connecting the rates of electrochemical reactions and overpotential. The Tafel equation was unique in that it could be applied

to irreversible electrochemical reactions that could not be described by thermodynamics. The several contributions he made in organic chemistry include reduction with amalgams and the Tafel rearrangement. Tafel is also known for introducing the hydrogen coulometer for measurement of electrochemical reaction rates and pre-electrolysis as a method for purifying solutions.

- . 본 강의록과 동영상에서 사용한 형태의 Butler-Volmer 방정식과 Tafel 방정식을 다음과 p. 8에 예시 함.

Electrochemical reaction kinetics

The big question: How much current do I achieve for the amount of overpotential that I apply?

Depends on two major factors (as with any chemical reaction):

- (1) The inherent kinetics of the reaction.
- (2) Effects of mass-transfer.

The Butler-Volmer Equation

$$i = i_o \left\{ \underbrace{\exp\left[\frac{\alpha_a n F \eta}{RT}\right]}_{\text{anodic term}} - \underbrace{\exp\left[-\frac{\alpha_c n F \eta}{RT}\right]}_{\text{cathodic term}} \right\}$$

$$i = i_a + i_c$$

i = current density
 i_o = exchange current density
 n = # of electrons transferred
 α = transfer coefficient (anodic or cathodic)
 F = Faraday's constant: 96,485 C/mol
 η = $(E - E_{\text{equil}})$ = overpotential
 R = gas constant
 T = temperature

- Assumes only one step is rate-determining
- If near equilibrium, both terms are important.
- If farther from equilibrium, one term dominates... can use the Tafel Equation!

$$i_a = i_o \exp\left(\frac{\eta}{b}\right)$$

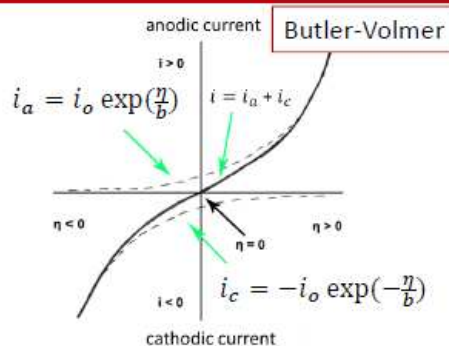
$$i_c = -i_o \exp\left(-\frac{\eta}{b}\right)$$

where b = Tafel slope

Electrocatalyst activity: Figures of merit


Four primary figures of merit for electrocatalyst activity:

- Exchange current density, i_o (mA/cm^2)
- Tafel slope, b (mV/decade)
- Current density at a given overpotential:
 $i_{E(\text{vs. RHE})}$ (mA/cm^2)
- Overpotential needed to reach a given current density:
 $\eta_{i=10\text{mA}/\text{cm}^2}$ (mV)



Three ways to report current densities:

- Per geometric area (cm^2_{geo})
- Per surface area ($\text{cm}^2_{\text{real}}$)
- Per electrochemically active surface area ($\text{cm}^2_{\text{ECSA}}$)
 - Closest to a true Turnover Frequency (TOF)

Easy/Practical

 Difficult/Useful

