Chapter 4: Passivity

Corrosion Engineering
ME 472
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Faraday’s Demonstration (1840s)

- **Observations:**
  - Fe does not corrode in concentrated nitric acid (HNO₃)
  - Fe corrodes in diluted nitric acid when a scratch is formed

- **Conclusion**
  - the concentrated nitric acid produced a protective film called passive film that protected iron against corrosion.
  - Scratching removed the protective film and allowed direct exposure of the bare metal surface to diluted nitric acid
Passivity

- Passivity: a condition of corrosion resistance due to the formation of thin surface films under highly oxidizing conditions (highly +ve cathodic reaction) at high anodic polarization ($\varepsilon_a$).
- Passive film: 1-10 nm in thickness
- Passive films are protective film only if:
  - Adherent
  - Dense and compact
  - Example: oxides such as $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, and $\text{Cr}_2\text{O}_3$ are very effective passive films.
• Adding >11%Cr to Fe to make stainless steels
  – Cr$_2$O$_3$ is stable over a wide range of potential and pH
  – Cr$_2$O$_3$ passive films provide corrosion resistance to stainless steels.
• The presence of a passive film will alter the anodic polarization behavior.
The anodic polarization curve for an active-passive metal consists of three regions:

1. Active region:
   - $i$ increases with $E$ until $E_{pp}$ (primary passive potential)
   - $i_{\text{crit}}$ is the maximum current

2. Passive region:
   - Above $E_{pp}$, the passive film forms and the corrosion current density drops to $i_{\text{pass}}$
   - $i_{\text{pass}}$ is very small in the passive state

3. Transpassive region:
   - the protective anodic film is damaged and may break down completely.
   - $i$ is proportional to $E$ in the transpassive region
Explanation of Faraday’s Experiment

- The cathodic half-cell potential in the concentrated nitric acid is highly positive and intersected the anodic curve in the passive region:
  - In the passive region
    - $i_{corr} = i_{pass}$. 

![Diagram of Faraday's experiment](image)
Diluting the solution by adding water reduced the pH and the half-cell potential to more negative value \((e = 1.229 - 0.059*pH)\) for the cathodic half-cell reaction and intersected the anodic curve in the active region. Scratching removed the passive film and \(i_{corr}\) is in the active region.
Effect of Environmental variables on Passivity

- The shape of the anodic curve and the range of the passive region is sensitive to the environmental conditions.
- Severe conditions of high acidity and temperature
  - decrease the passivity region
  - increase $i_{\text{pass}}$
  - Increase $E_{\text{pp}}$
  - Increase $i_{\text{crit}}$

![Graph showing the effect of increasing acid concentration and temperature on passivity.](image)
Effect of Oxidizer Concentration

- Consider different cathodic reactions from 1 to 8.
- The oxidizing power increases with increasing $e_c$. This means that the solution becomes more corrosive going from 1 to 8.
- As the half-cell potential of the cathodic reaction becomes more positive, $i_{corr}$:
  - increases from A to C (in the active region)
  - drops to D (in the passive region)
  - Increase from E to F (transpassive region)
Remember the Effect of solution velocity for an active-metal

**FIGURE 3.13** Effect of stirring during combined polarization: (a) on $i_L$, (b) on $i_{corr}$. 
Effect of solution velocity
active-passive metal

- Assume the catholic reaction is aerated water under concentration polarization and intersects the anodic curve in the passive region.
- Increasing the solution velocity:
  - Corrosion rate increases from 1 to 3 (active anodic behavior)
  - Corrosion rate drops to 4 and becomes independent of velocity (passive anodic behavior) where \( i_{\text{corr}} = i_{\text{pass}} \)
FIGURE 3.13  Effect of stirring during combined polarization: (a) on $i_L$, (b) on $i_{corr}$.
Criterion for Passivity

- To produce anodic passive behavior, the critical current density ($i_{\text{crit}}$) must be exceeded.
- The anodic potential must be maintained in the passive region without falling back in the active region or getting into the transpassive region.
- A high current density is required to cause passivation initially ($> i_{\text{crit}}$)
- But only a small current density is required to maintain it ($i_{\text{pass}}$)
- After passivation, the corrosion rate corresponds to small passive current density ($i_{\text{corr}} = i_{\text{pass}}$).
Criterion for Passivity

- Excellent passivating alloy:
  - Lower $i_{\text{crit}}$
  - More active (-ve) $E_{\text{pp}}$
  - Low $i_{\text{pass}}$

- Not good passivating alloy:
  - High $i_{\text{crit}}$
  - More anodic (+ve) $E_{\text{pp}}$
  - High $i_{\text{pass}}$
Criterion for Passivity

- An active-passive metal can be forced in the passive region by using oxidizers (strong cathodic reactions) such as strong acids (nitric acid as in Faraday’s experiment).
- Very few metals will passivate in weak oxidizers (weak acids). A good example is titanium which readily passivates even in weak acids or aerated water.
- Steel requires a strong oxidizing agent, such as fuming nitric acid, for its passivation (remember Faraday’s experiment).
• **Measurements of anodic polarization curves:**
  - Two variables: current \( i \) and potential \( E \)
  - Two types of experiments:
    - Vary the current (independent variable) and measure the potential (dependent variable). This is called galvanostatic polarization.
    - Vary the potential (independent variable) and measure the current (dependent variable). This is called potentiostatic polarization.
  - Polarization curves for active metals can be obtained by either method.


- **Galvanostatic Approach:**
  - Increase the current and measure the resulting shift in potential.
  - 3-electrode cell.

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**Galvanostat**

Source of e.m.f. \( E \)

Galvanometer \( V \)

Voltmeter

Counter (auxiliary) electrode

Saturated calomel reference electrode

Working electrode

Electrolyte

Not suitable approach
Experimental Measurement of active-passive Polarization

- **Potentiostatic Approach:**
  - Shift the metal potential in the anodic direction (positive) and measure the current required to cause that shift.
Potentiostatic Anodic Polarization of Iron and Stainless steel

• Alloying with a more easily passivated metal normally increases the ease of passivation and lowers the passivation potential, as in the alloying of iron and chromium.

• Anodic polarization curve for Fe and Fe-10.5%Cr in 1 N sulfuric acid (H₂SO₄).

![Anodic polarization curve diagram]
Alloy Evaluation

- Potentistaic polarization curves of the alloys can be used to select the best alloy in a given corrosive environment.
  - Example: you have 4 possible alloys to be used. Which one will provide more corrosion resistant in a given solution?
    - The best alloy in solution 1 is
    - The best alloy in solution 2 is
    - The best alloy in solution 3 is

FIGURE 4.16  Schematic anodic polarization curves for hypothetical alloys A, B, C, and D, illustrating evaluation in various chemical conditions: 1, reducing; 2, moderately oxidizing; 3, highly oxidizing.
Alloy Evaluation

• Alloying with a more easily passivated metal normally increases the ease of passivation and lowers the passivation potential.

• Each alloy system has to be evaluated for its own passivating behavior as illustrated by the case of three Ni alloys:
  – Alloy B shows little passivation feature
  – Alloy C shows low $i_{\text{crit}}$ and active $E_{\text{pp}}$, but $i_{\text{pass}}$ increases in the passive region
  – Alloy C-276 is the best and shows constant $i_{\text{pass}}$ in the passive region
    • Solution: sulfuric acid and 0.25 M potassium sulfate.

<table>
<thead>
<tr>
<th>B</th>
<th>Ni-25%Mo</th>
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<tbody>
<tr>
<td>C</td>
<td>Ni-15%Cr</td>
</tr>
<tr>
<td>C276</td>
<td>Ni-15%Cr-16%Mo</td>
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Solution Corrosivity

- Measuring the anodic polarization curve of an alloy in different solutions will give indication of the corrosivity of the solution.
- Example: compare the corrosivity of \((1 \text{ N } \text{H}_2\text{SO}_4)\) and \((1 \text{ N } \text{H}_2\text{SO}_4 + 1 \text{ M NaCl})\) using Hastelloy C and a stainless steel.
- This shows the detrimental effect of Cl\(^-\).
Anodic Protection

- The corrosion rate of an active-passive metal can be reduced by shifting the potential of the metal so that it is in the passive range. Two ways to shift the potential:
  - Use a strong oxidizer
  - Use external power supply
- Using an external power supply to shift the potential in the passive region is called anodic protection.
  - $E = E_1$ before protection
  - $E = E_2$ after anodic protection
**E vs $i_{\text{app}}$ in anodic potential**

![Graph showing E vs log(i) with various points and lines labeled E, E$_{corr}$, E$_1$, E$_2$, E$_3$ with corresponding currents $i_{app}$, $i_a$, $i_c$, $i_{pass}$, $i_{corr}$, $i_{a1}$, $i_{c1}$, $i_{a2}$, $i_{c2}$, $i_{pass}$, $i_{c3}$ and values indicating equilibriums.]

<table>
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<tr>
<th>$E$</th>
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<td>$i_{c1}$</td>
<td>$i_{a1} - i_{c1}$</td>
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<tr>
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<td>$i_{a2}$</td>
<td>$i_{c2}$</td>
<td>$i_{a2} - i_{c2}$</td>
</tr>
<tr>
<td>$E_3$</td>
<td>$i_{pass}$</td>
<td>$i_{c3}$</td>
<td>$i_{pass} - i_{c3}$</td>
</tr>
</tbody>
</table>
Anodic Protection

- The current required to achieve protection ($i_{\text{crit}}$) is several orders of magnitudes higher than the current required to maintain it ($i_{\text{pass}}$)
- Limited use mainly in:
  - Protecting steel tanks in strong acids
  - Protecting stainless steel heat exchanger tubes
Anodic Protection

- The metal to be protected is made the anode in an electrolytic cell.
- The metal to be protected is connected to the + pole of a power supply.
- Example: anodic protection of a tank containing an acid is shown.
- The cathode is usually a high resistant corrosion electrode such as platinum-clad brass or stainless steels.
10.7 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current which can be used to do work. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the − sign of the anode is where the electrons leave the cell.

10.8 In an electrolytic cell, electrons are forced through the circuit by an external source. Although the cathode is still the site of reduction, it is now the negative electrode whereas the anode, the site of oxidation, is positive.
Anodic Protection

• Requirements of anodic protection
  – Active-passive metal
  – Broad range of passivity
  – Low $i_{\text{pass}}$
  – Availability of power supply To provide needed $i_{\text{app}}$
  – Continuous monitoring of potential

• Disadvantages:
  – Applicable only for passive metals
  – High current needed initially to induce passivity ($i_{\text{app}}>i_{\text{crit}}$)
  – High $i_{\text{corr}}$ if the power is failed
  – High cost of installation and monitoring and power
Anodic Protection

- The main advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements.
- Anodic protection has been most extensively applied to protect equipment used to store and handle sulfuric acid and to anodically protected heat exchangers used to cool sulfuric acids in sulfuric manufacturing plants.
- These heat exchangers are sold complete with the anodic protection systems installed and have a commercial advantage in that less costly materials can be used.