



# Electrochemistry

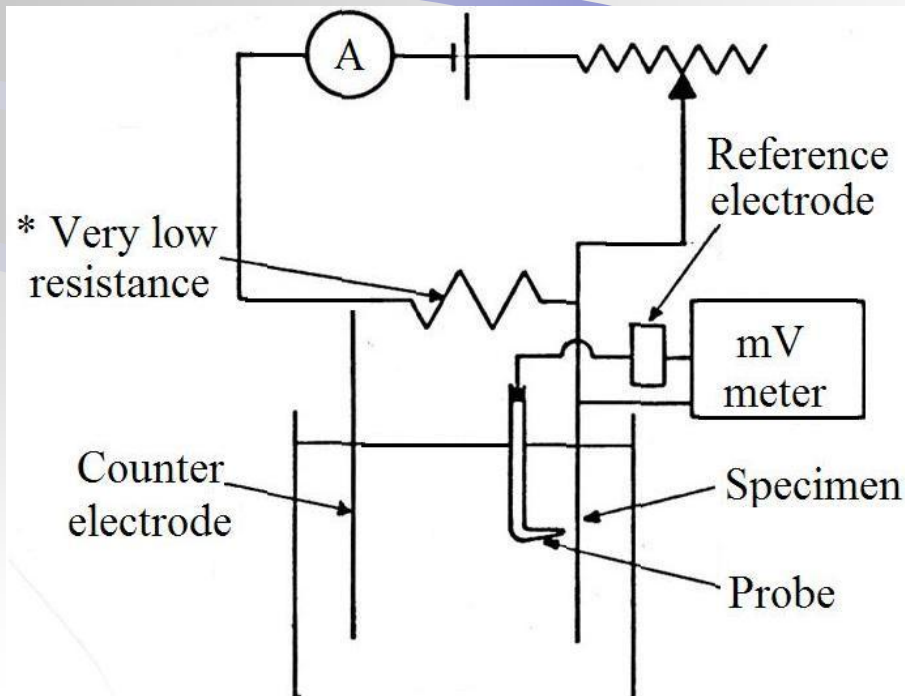
CHEM 5390

**CHEM 5390**

# Electrochemical Measurements for Corrosion

## Corrosion Measurements

Involve the use of a potentiostat for applying a potential (relative to a reference electrode) and measuring the current (flowing from the working electrode to the counter or auxiliary electrode). The working electrode typically having the corroding surface.



# Electrochemical Measurements for Corrosion

Measurements can be destructive or non-destructive.

## Destructive

Linear Polarization Method

Measures polarization resistance –  $R_p$

Potentiodynamic Polarization

Cyclic Polarization

Cyclic Pitting Scans

Weight Loss Method

Open Circuit vs Time Studies

## Non-destructive

Linear Polarization Method

Electrochemical Impedance

Spectroscopy (EIS)

# Electrochemical Measurements for Corrosion

## Linear Polarization Method

Valid for corrosion under activation control.

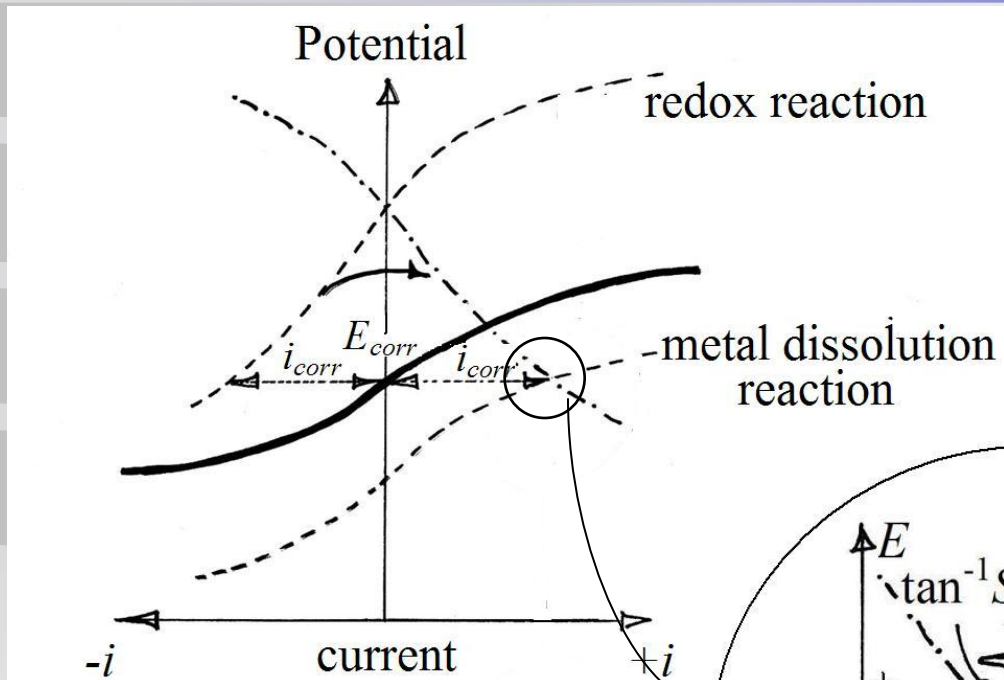
Involves applying a small perturbation to the potential around  $E_{corr}$  (i.e.,  $\pm \Delta E \approx 10$  mV).

Slope of summed curve (measure  $E$  vs  $i$  for system) is difference between slopes of curves for the coupled reactions:  $S_a - S_c$

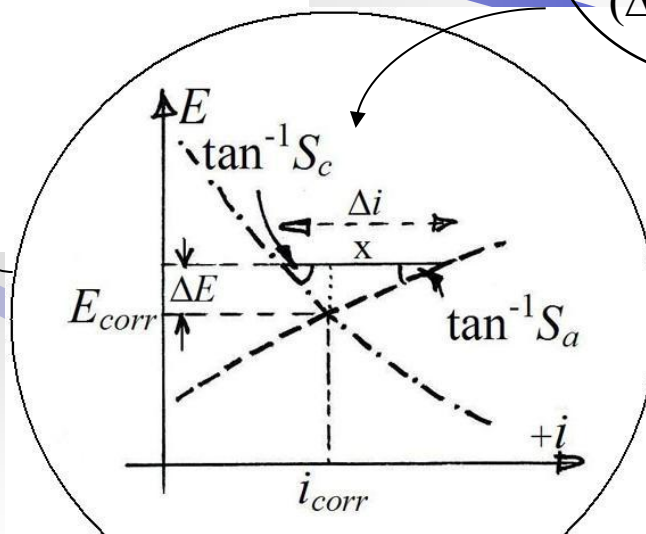
Gives polarization resistance -  $R_p$

# Electrochemical Measurements for Corrosion

## Linear Polarization Method



N.B.  $\Delta i$  for summed curve  
 $= i_a + |\Delta i_c|$   
( $\Delta i_a = x$ )



# Electrochemical Measurements for Corrosion

## Linear Polarization Method

The curves are ~linear within ~20mV –  $S_a$  and  $S_c$  are constant. For  $\Delta E$  around  $E_{corr}$ ,  $S_a$  and  $S_c$  are related to  $i_{corr}$  (the required quantity): assuming the high-field approximation for the individual reactions.

$$\left. \frac{dE}{di} \right|_{anodic} = S_a = \frac{b_a}{2.303i_{corr}} \quad \left. \frac{dE}{di} \right|_{redox} = S_c = \frac{b_c}{2.303i_{corr}}$$

$$\text{slope } S_a = \frac{\Delta E}{x}$$

$$\text{slope } S_c = \frac{\Delta E}{\Delta i - x}$$

$$\therefore \frac{\Delta E}{\Delta i} = \frac{S_a - |S_c|}{S_a |S_c|} \quad \text{or } i_{corr} = \frac{1}{2.303} \frac{b_a |b_c|}{b_a + |b_c|} \cdot \frac{\Delta i}{\Delta E}$$

Polarization Resistance ..Rp =  $\Delta E / \Delta i$  .. is measured,  $V = iR$ . The Tafel coefficient  $b_a$  and  $b_c$  must be known. (?)

# Electrochemical Measurements for Corrosion

## Linear Polarization Method

Polarization Resistance  $R_p = \Delta E / \Delta i$  is measured,  $V = iR$ . The Tafel coefficient  $b_a$  and  $b_c$  must be known. Can instead use for potentiodynamic polarization curves.

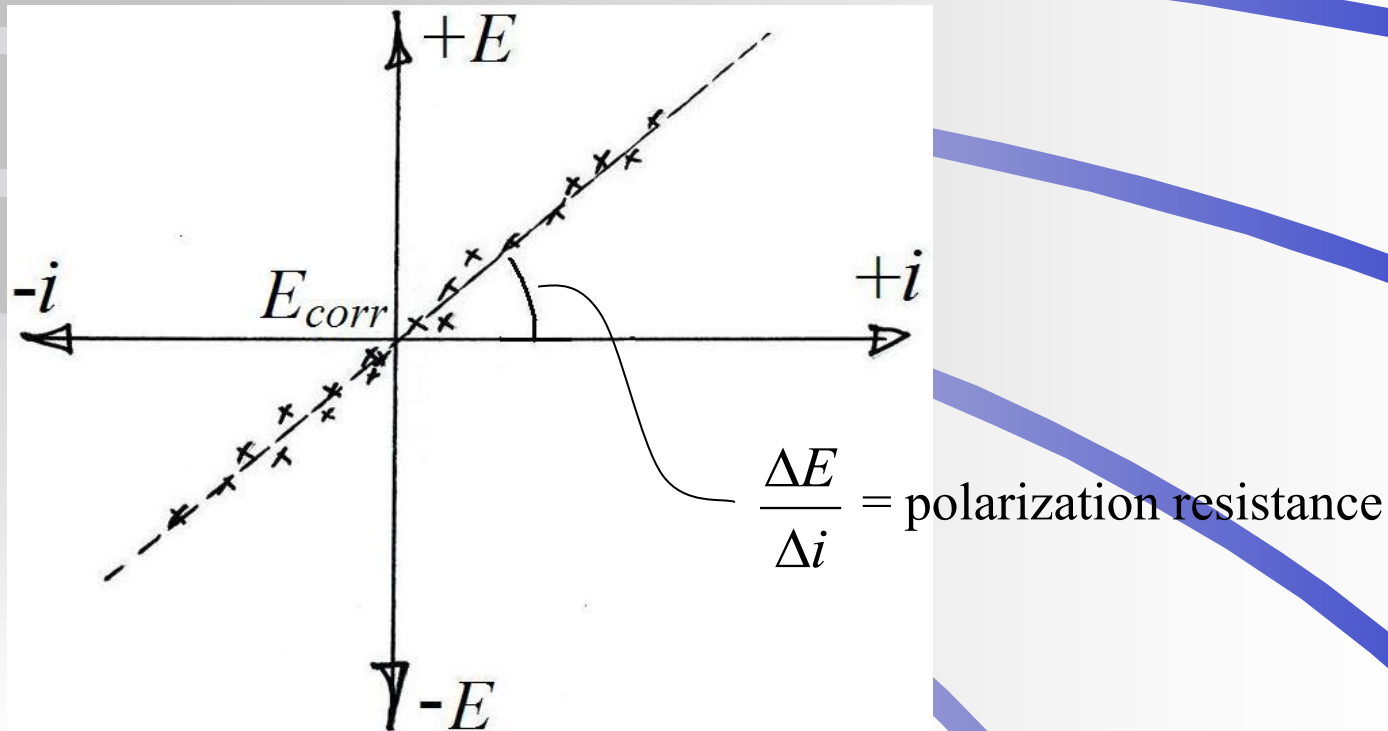
Stern-Geary Equation:

$$i_{corr} = \frac{1}{2.303} \frac{b_a |b_c|}{b_a + |b_c|} \cdot \frac{\Delta i}{\Delta E}$$

# Electrochemical Measurements for Corrosion

## Linear Polarization Method

Remember: during linear polarization measurements plot  $E$  vs  $i$  (not  $\log i$ ) around the corrosion potential:



# Electrochemical Measurements for Corrosion

## Linear Polarization Method (Helpful Hints)

- Involves the application of low over-potentials and therefore the currents are relatively very small. This means that the charging current (capacitance current) can make a significant contribution to the noise or background current.
- Use very slow scan rates and perform a separate cyclic scan to check whether you are measuring capacitance.

(0.1667 mV/s)

- The reverse scan should produce an  $iE$  curve that retraces over the forward recorded  $iE$  curve.
- The  $iE$  curve can be curved due to a difference in the anodic and cathodic Tafel slopes.

# Electrochemical Measurements for Corrosion

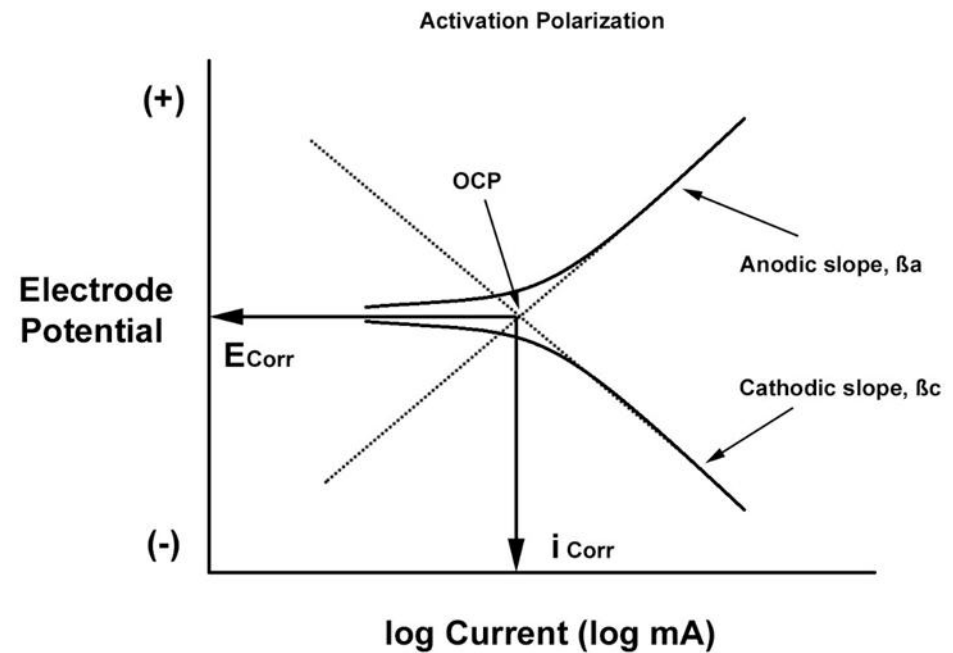
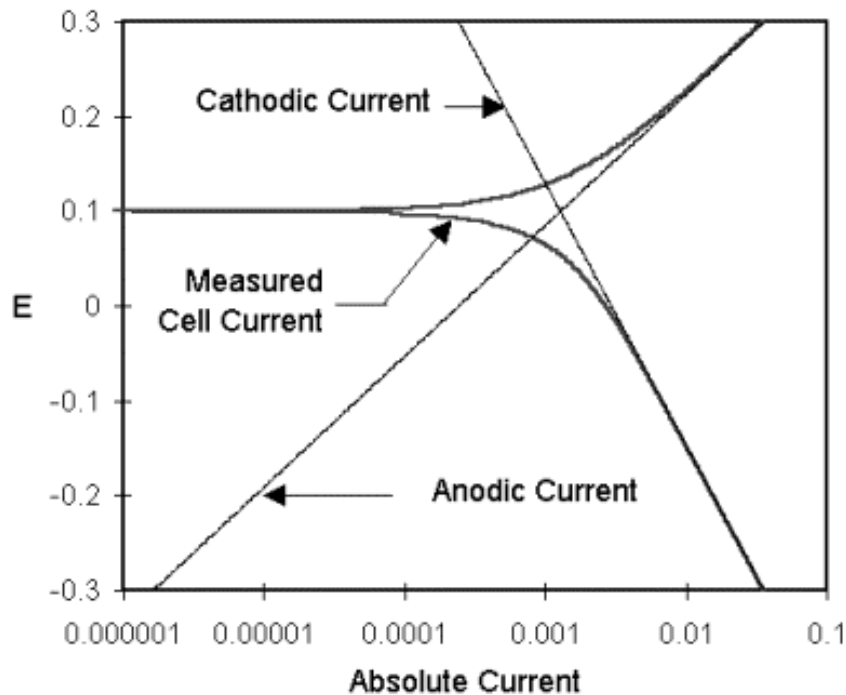
## Linear Polarization Method (Helpful Hints)

- It is important to view the  $iE$  curve. If the  $iE$  curve is curved, the polarization resistance can be obtained by drawing a line that is tangential to the curve at  $E_{\text{corr}}$  and at zero current.
- Some portable instruments use a potential-step method. In this case the current, at, for example,  $-10$  mV and  $+10$  mV is measured and  $R_p$  is computed from these measurements.
- The advantage of this technique is that the current measurements are made at a constant voltage and therefore the charging current is zero.
- The disadvantage is that no  $iE$  curve is recorded and therefore an error can be introduced if there is curvature in the  $iE$  graph.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

(Tafel – from Butler-Volmer Equation)



# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

### Destructive Technique

Can measure the net current across the electrode – at the corrosion potential there is no net current (only local anode – cathode currents which constitute the corrosion current).

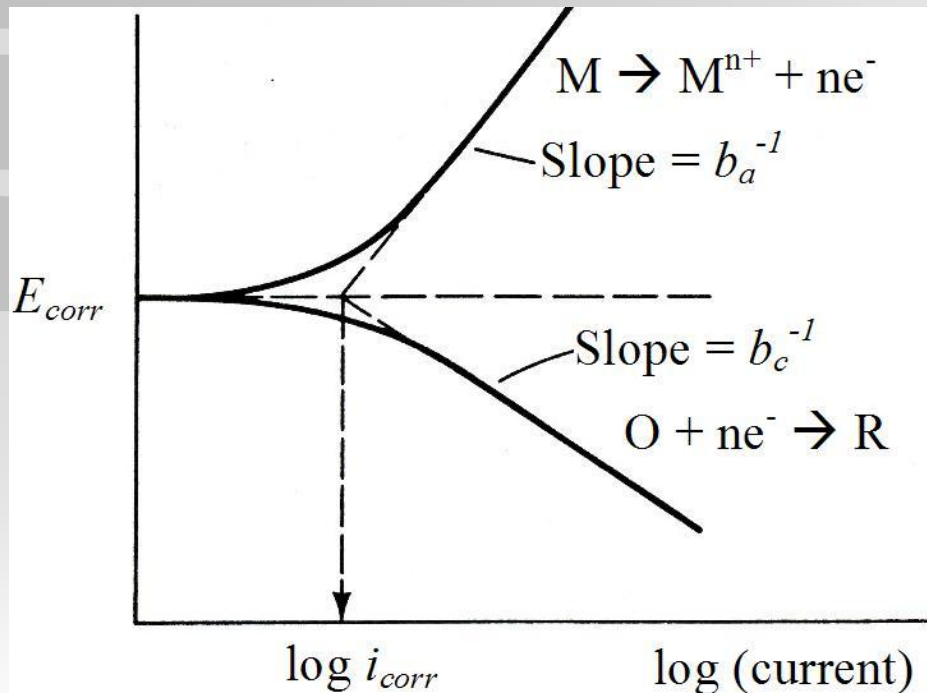
We cannot measure corrosion rate directly, but  $i_{corr}$  can be calculated from Stern-Geary equation or by other methods.

$$i_{corr} = \frac{1}{2.303} \frac{b_a |b_c|}{b_a + |b_c|} \cdot \frac{\Delta i}{\Delta E}$$

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

Measure potential and current at some distance on either side of  $E_{corr}$  – extrapolate  $E - \log i$  curves (in same quadrant) back to  $E_{corr}$  ...

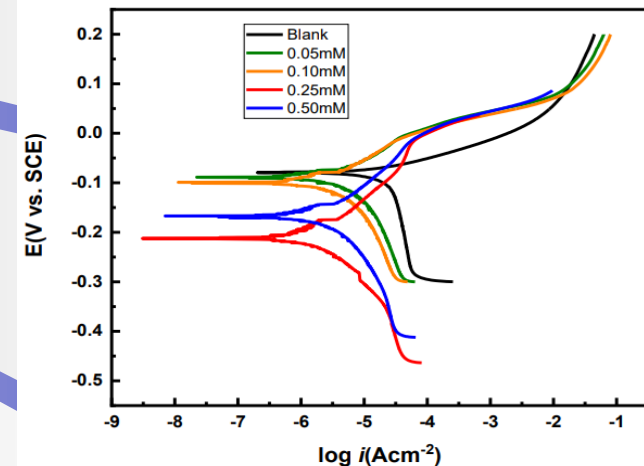
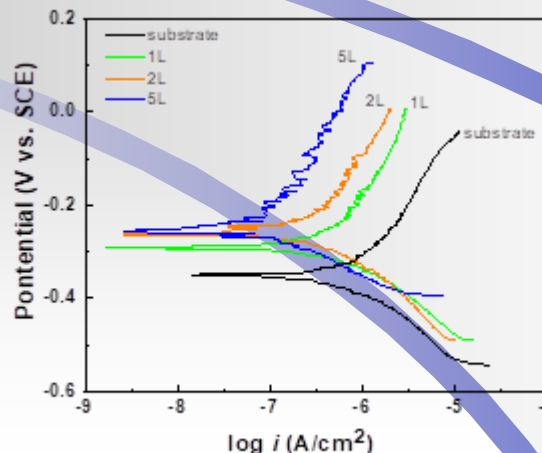
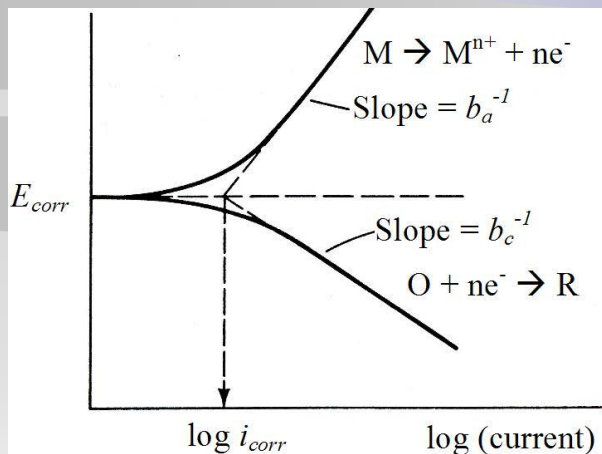


Plot of the total current ( $i_T = i_o + i_c$ ) versus potential showing the extrapolation of the Tafel regions to the corrosion potential,  $E_{corr}$ , to yield the corrosion current,  $i_{corr}$ .

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

The graphing method and also the Stern-Geary equation assumes there is only one reaction occurring at the cathode and one occurring at the anode. Sometimes this is not a good assumption.



# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

To obtain a more accurate estimation of  $i_{corr}$ , the cathodic polarization region can be used since the anodic region can contain additional reactions or current density oscillations.

In the plot, a horizontal line is drawn at the  $E_{corr}$  value and another horizontal line drawn 100 mV cathodic from  $E_{corr}$ .

A slope line is drawn from the 100 mV meeting point on the cathodic branch to intersect with the  $E_{corr}$  line.

The point of intersection is taken as the value of  $i_{corr}$

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization (Helpful Hints)

- Involves measurements at high over-potential in which  $\log i$  is recorded.
- The best method of performing these measurements is by :
  - 1) Using two identical electrodes and recording the anodic curve on one electrode and the cathodic curve on the other electrode. In each case starting at the open circuit potential  $E_{ocp}$  (or  $E_{corr}$ )
  - 2) Performing the cathodic curve on one electrode starting the scan from  $E_{ocp}$ . Turning off the potentiostat and monitoring  $E_{ocp}$  until it returns to its original value. The anodic scan is then recorded again starting at the  $E_{ocp}$ .
  - 3) Some instrumental software will do this for you – just check to make sure how it is running the experiments.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization (Helpful Hints)

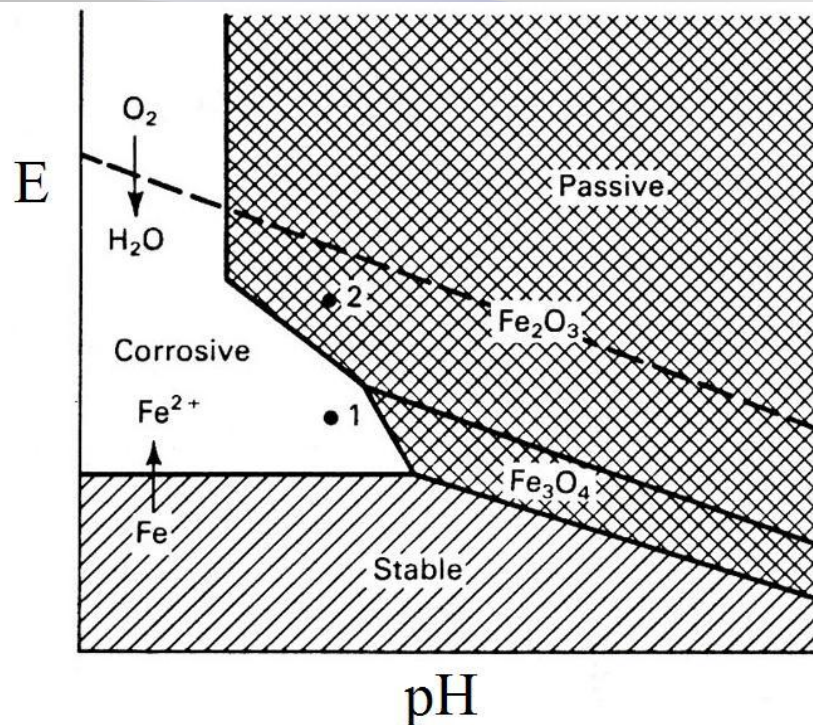
- Before running a measurement, it is best to allow the metal electrode to reach a steady state potential. This can be observed by performing a potential time measurement in which  $E_{\text{corr}}$  is monitored with time.
- Scan Rates must be slow normally in the range of 0.1 mV/s  
The cathodic plot is scanned to an over-potential of about 200-400 mV (we use 250 mV in our lab).
- Anodic potentials can be scanned much higher depending on what information needs to be obtained.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

Under certain conditions of potential and pH, some metals form protective films, i.e., they passivate.

### Passivation



Pourbaix diagram for the iron/water/dissolved oxygen system showing the effect of potential in moving the system from a corrosive (active) region (point 1) to a passive region (point 2)

Can exam the kinetics using a potentiodynamic scan and Evans diagram.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

### Passivation

A loss of electrochemical reactivity (drastic decrease in corrosion rate) that many alloys (e.g. stainless steel, Ni-based alloys, Al alloys) exhibit under certain environmental conditions.

- Passivation usually is the result of the presence of a thin protective oxide or oxy-hydroxide passive film on the metal surface.
- However, passive metals are susceptible to local breakdown and accelerated localized attack.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

### Passivation

Passive films are a 3-dimensional oxide or oxyhydroxide, usually nm in thickness, that acts as a barrier between the metal and the electrolyte.

Could be a bilayer structure with a porous or hydrated deposit layer on top of barrier layer.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

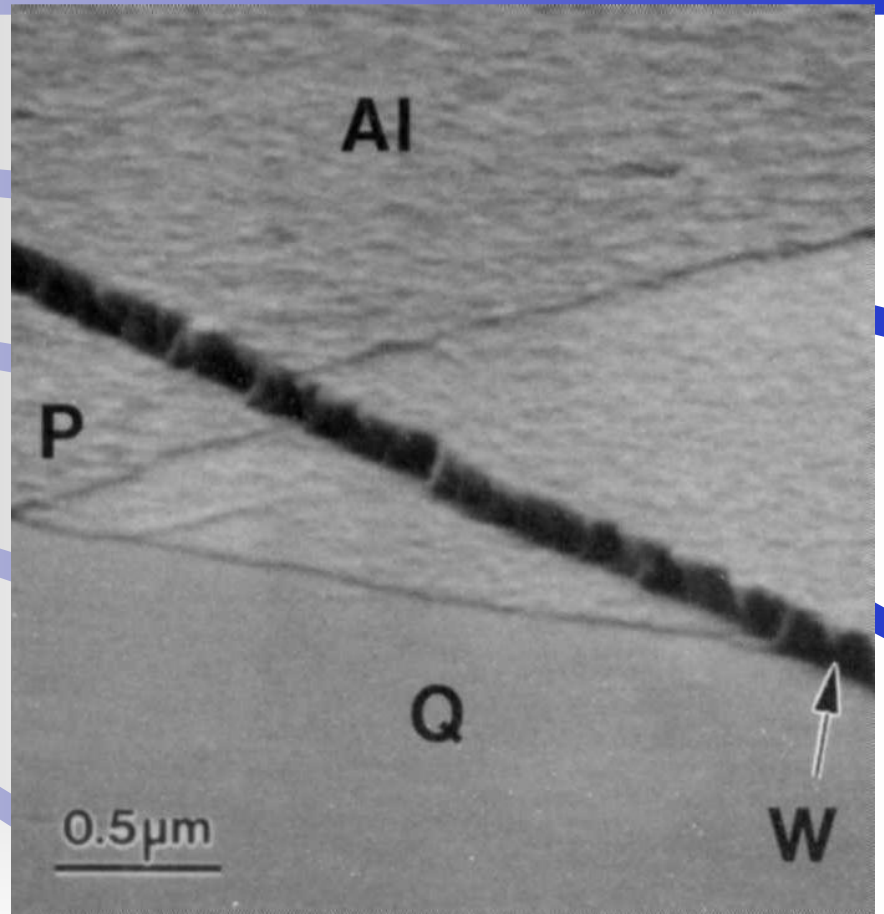
### Passivation

Example

Passive Oxide Layer on  
Al Thin Film

Sample was 150-nm thick Al film  
on quartz substrate (Q).

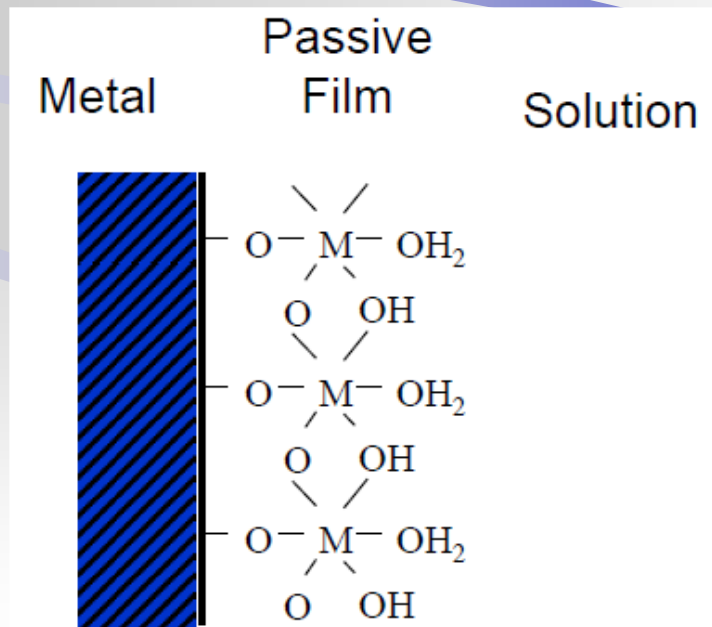
Pit in thin film caused undermining  
of passive film (P) at pit wall (W)  
undermined passive film is  
lying on substrate surface.



# Electrochemical Measurements for Corrosion

## Passivation

- Composition and thickness of the passive film are functions of potential and solution composition.
- For alloys, usually one element is enriched in the film (films on Fe-Cr alloys are enriched in Cr).
- Passive films can be either crystalline or amorphous.
- Films can be either insulators (e.g., Al, Ti, and Ta) or semiconductors (e.g., Fe and Ni).

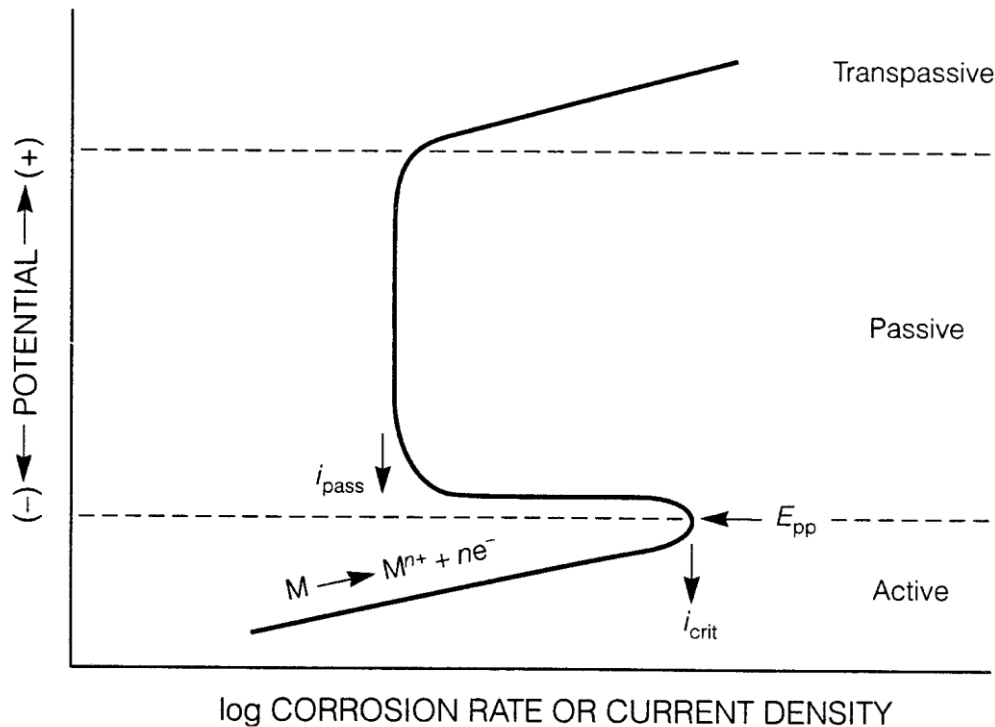


# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

### Passivation

Distinctive potential-current behavior of a passive metal:



Schematic active-passive polarization behavior.

- $i_{pass}$  - passive current density
- $E_{pp}$  - primary passivation potential
- $i_{crit}$  - critical current density
- $E_{trans}$  - transpassive potential

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

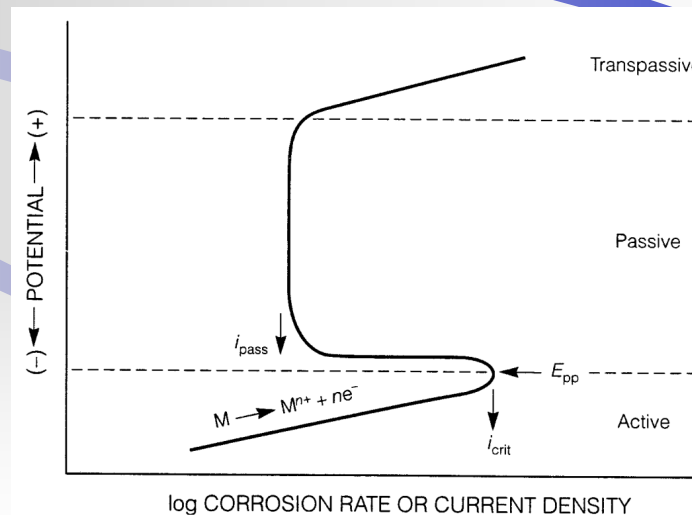
### Passivation

At the active-passive transition, the current density can decrease by many orders of magnitude.

The current density in the passive region,  $i_{\text{pass}}$ , is often relatively independent of potential.

Passive films may break down at the very high potentials, allowing high currents to pass again. This is called the transpassive region.

Transpassive current may be associated with oxygen evolution or dissolution - it is different from currents associated with pitting.



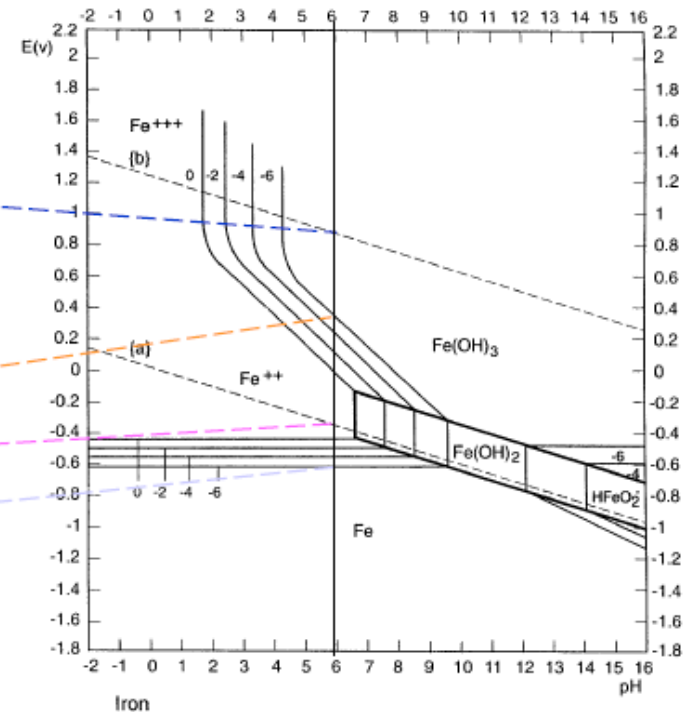
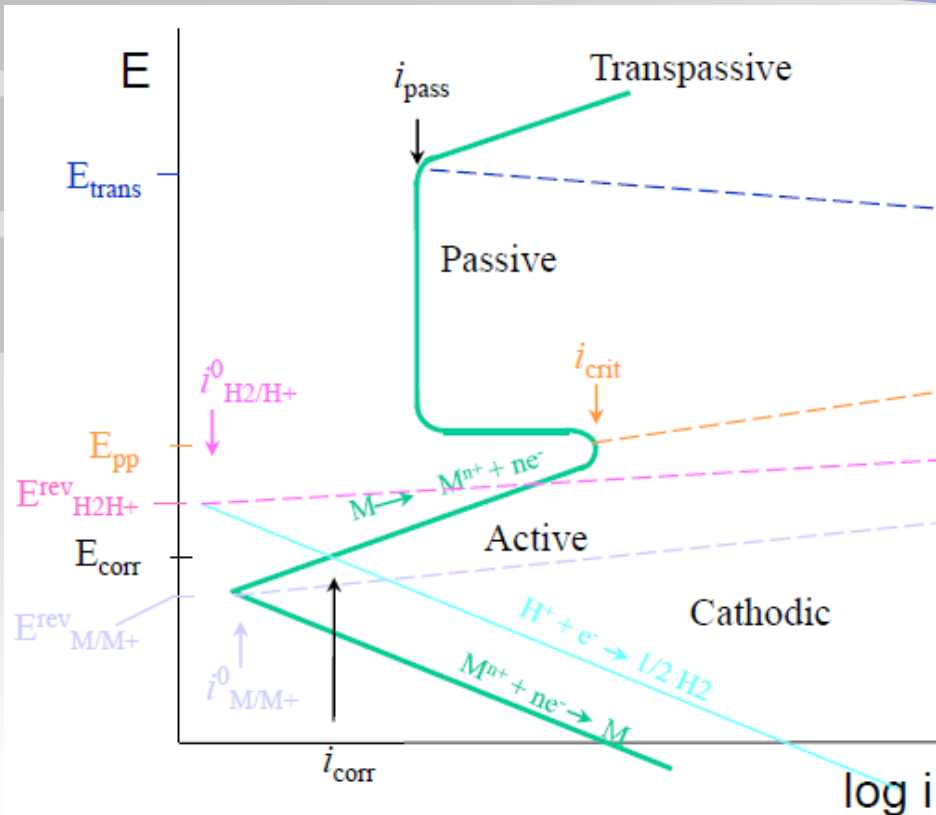
Schematic active-passive polarization behavior.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

### Passivation

For certain systems, the critical potential values observed in measured polarization curves may relate to boundaries in the related Pourbaix diagram:

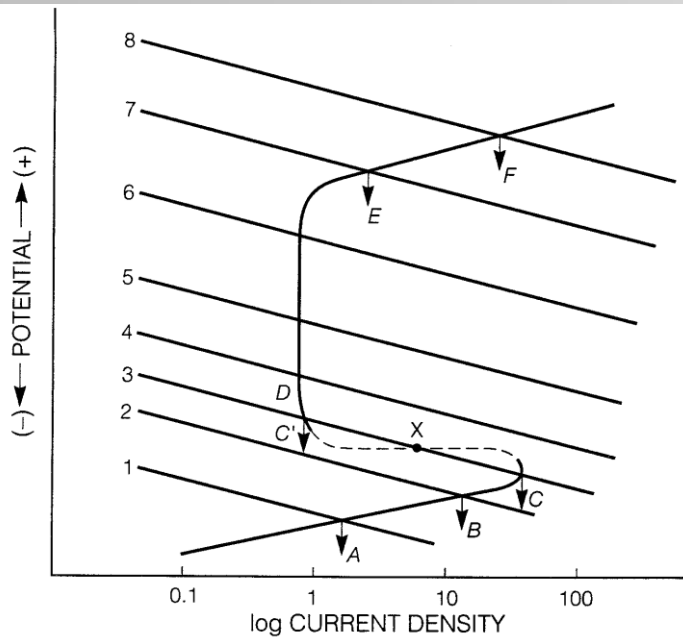


# Electrochemical Measurements for Corrosion

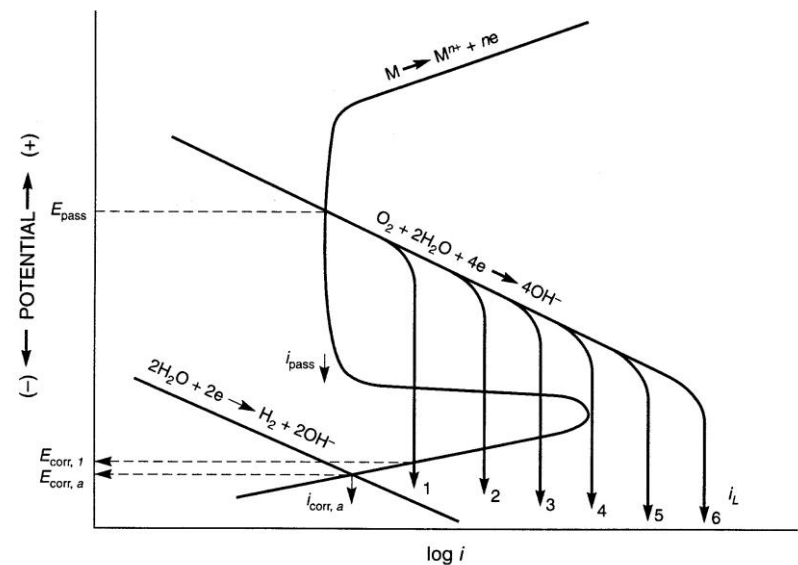
## Potentiodynamic Polarization

### Passivation

The measured polarization curve can take different forms depending on the relative positions of the anodic and cathodic half reactions:



Effect of oxidizer concentration on corrosion of an active-passive alloy.



Effect of deaeration, aeration, and stirring on corrosion of active-passive stainless steel in neutral saltwater.

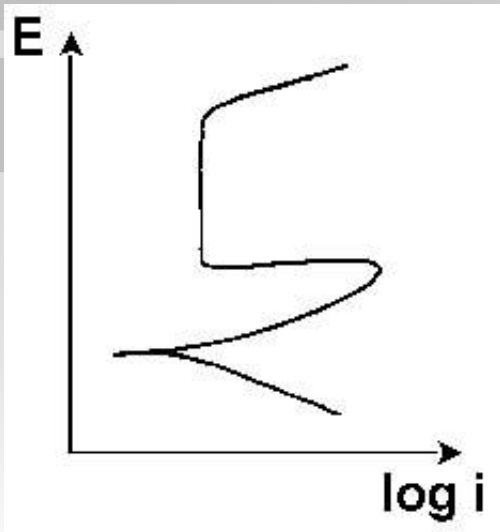
# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

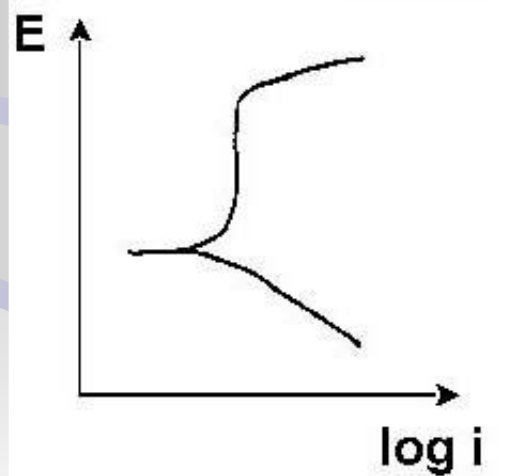
### Passivation

The measured polarization curve can take different forms depending on the relative positions of the anodic and cathodic half reactions:

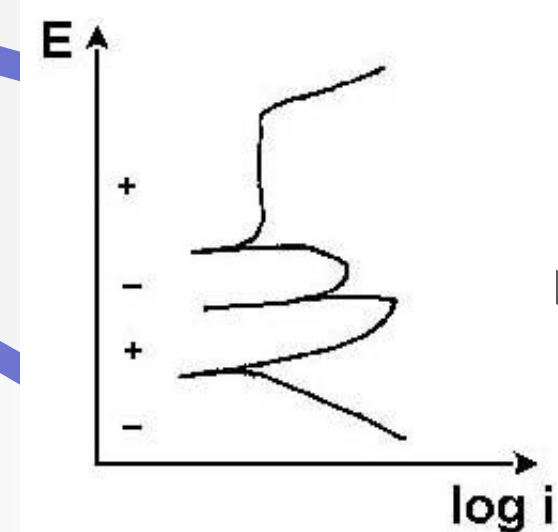
Active-passive



Spontaneously passive



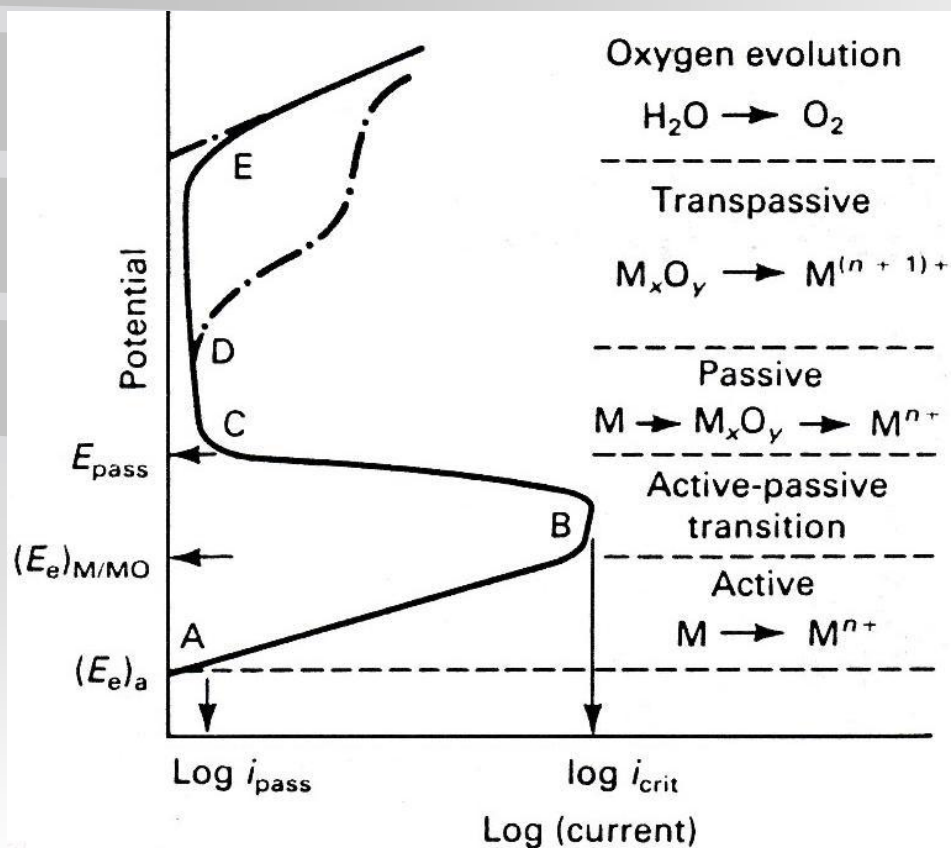
Unstable passivity



# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

The polarization curve for the anodic reaction of a passivating metal drawn for potentials more noble than the equilibrium potential  $(E_e)_a$



Oxidative dissolution of oxide (e.g.,  
 $\text{Cr}_2\text{O}_3 \rightarrow \text{CrO}_4^{2-}$ )

$(E_e)_{\text{M/MO}}$  is the equilibrium potential  
for oxide/hydroxide formation

Tafel region

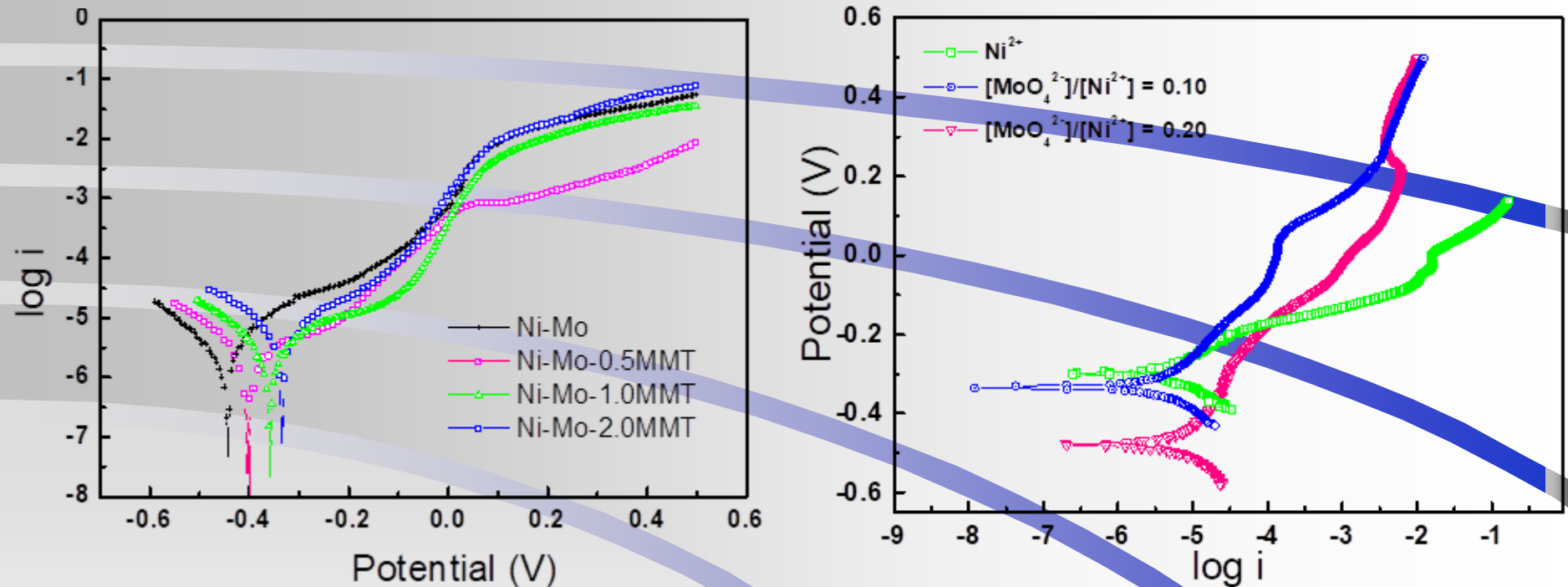
( $i_{\text{crit}}$  is min. reaction rate required to  
**initiate** film growth by precipitation  
of  $\text{M}^{n+}$ )

There is a cyclic method also.

# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

- Examples



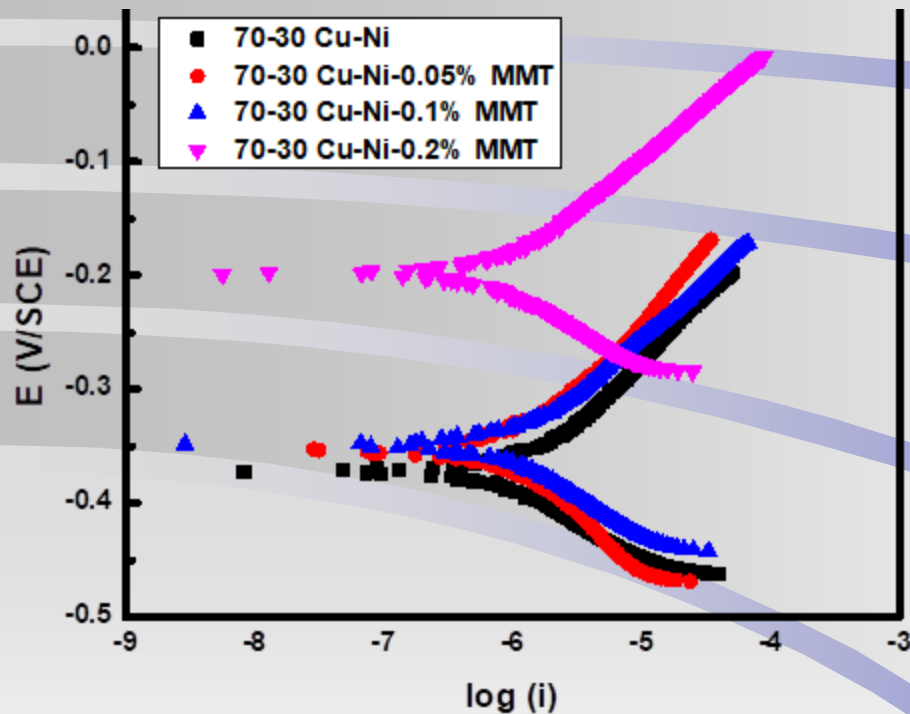
**Figure 7.** Potentiodynamic polarization curves of Ni-Mo and different Ni-Mo-MMT nanocomposite coatings after 24h immersion in 3.5% NaCl solution.

**Figure 7:** Tafel plot and anodic polarization of nickel-molybdenum alloy in 3.5 (w/v) % NaCl solution. The alloys were electrodeposited from plating solutions at different  $[\text{MoO}_4^{2-}]/[\text{Ni}^{2+}]$  molar ratios of 0.1, 0.15, and 0.2 compared to nickel deposit.

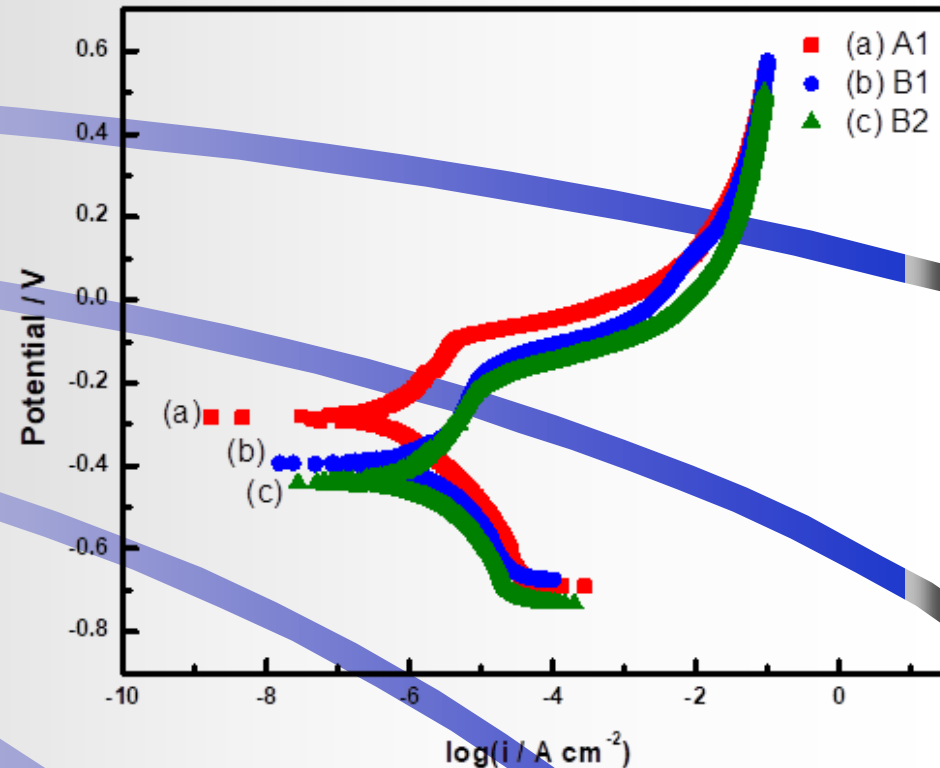
# Electrochemical Measurements for Corrosion

## Potentiodynamic Polarization

- Examples



**Fig. 7.** Tafel plots for the 70-30 Cu-Ni coatings with and without MMT after being immersed in a 3.5 % NaCl solution for 2 weeks.



**Figure 4.** Potentiodynamic polarization curves for the fresh Nickel coatings (a) A1 (squares), (b) B1 (circles), and (c) B2 (triangles) run in 3.5 % NaCl.

# Electrochemical Measurements for Corrosion

## Cyclic Pitting Scans

- The technique is used to evaluate the susceptibility of metals to pitting corrosion in a particular environment. It is applicable to metals such as stainless steels, high nickel alloys and aluminium, which form a passive protective film.
- With this technique, the potential is scanned to voltages in the transpassive region.
- Exceeding the passive region is indicated by a sudden increase in current. At this stage the voltage scan is reversed, usually when the current reaches a certain current density ( $0.5 \text{ mA cm}^{-2}$ )

# Electrochemical Measurements for Corrosion

## Cyclic Pitting Scans

- The extent of the hysteresis in the reverse scan is an indication of the susceptibility to pitting corrosion.
- Pitting corrosion is considered to stop at the potential where the  $iE$  curve from the reverse scan crosses the  $iE$  curve of the forward scan.

# Electrochemical Measurements for Corrosion

## Cyclic Pitting Scans

- The sudden increase in current can be due to three processes:
  - 1) Onset of pitting corrosion
  - 2) Trans-passive uniform corrosion
  - 3) The oxygen evolution reaction
- In the case of trans-passive corrosion, the slope of the  $iE$  curve is not as steep compared to pitting corrosion and oxygen evolution.
- In the case of oxygen corrosion, the reverse  $iE$  curve normally will retrace over the forward  $iE$  curve.

# Electrochemical Measurements for Corrosion

## Weight Loss Testing

### Destructive

Take coupons (4.0 cm × 4.0 cm) bare or coated. Record the initial weight of the dried coupons. Immerse samples in corroding solution at certain temperature and time.

After immersion time, remove coupons from solution. (Corrosion products may be removed from the surface by hard brushing followed by sonication in water and ethanol).

Finally, weigh cleaned and dried sample to calculate the total weight loss. Average weight loss from the experiments used to calculate the final weight loss and corrosion rates.

# Electrochemical Measurements for Corrosion

## Weight Loss Testing

The corrosion rates (CR) and inhibition efficiencies (IE) are calculated from weight loss data using the following equations:

$$CR = \frac{W_i - W_f}{AT}$$

$$IE\% = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100$$

$W_i$  (g) is the initial weight of the coupons,  $W_f$  (g) is the weight after the immersion tests,  $A$  (m<sup>2</sup>) is the surface area and  $T$  (h) is the immersion time.

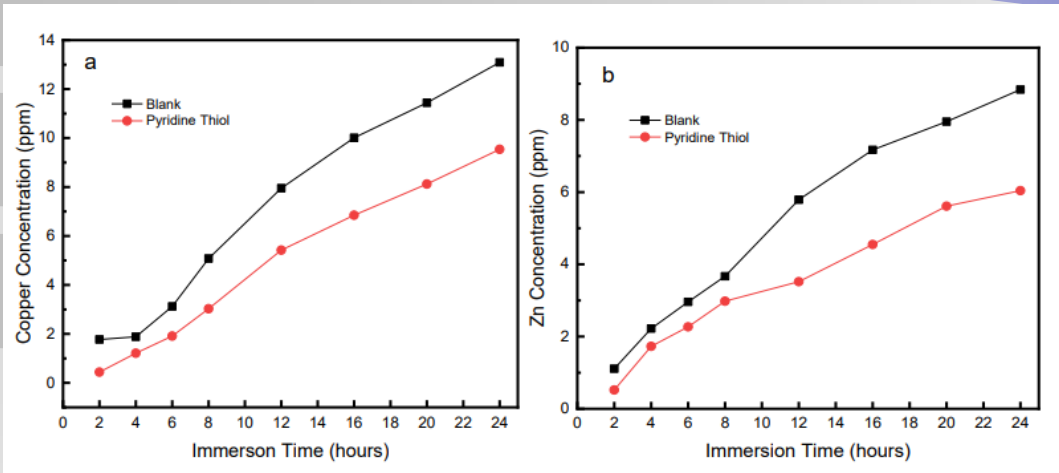
$CR_{inh}$  and  $CR_{blank}$  are the corrosion rates with and without the inhibitor in solution.

# Electrochemical Measurements for Corrosion

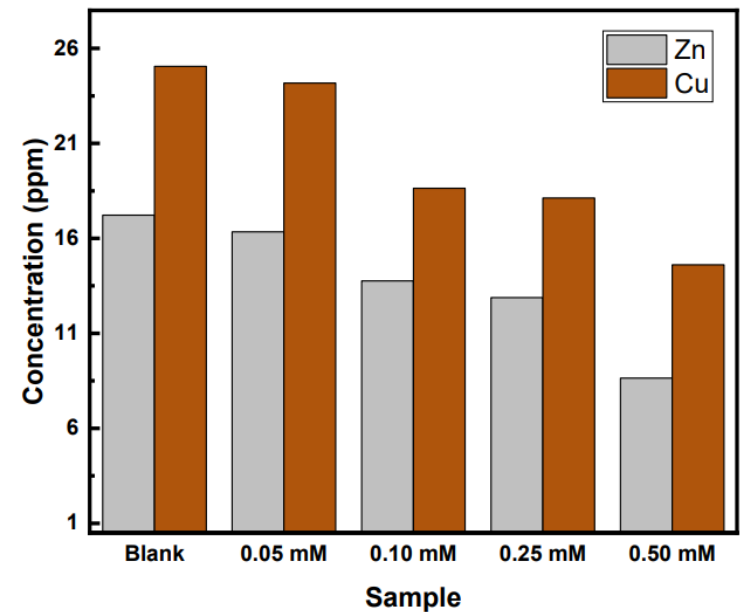
## Weight Loss Testing

A good technique to pair with weight loss testing is AAS or ICP-MS.

For example, looking at copper and zinc loss from our samples:



**Figure 2.** Copper (a) and Zinc (b) concentration (ppm) present in 0.5 M  $\text{H}_2\text{SO}_4$  solution with respect to immersion time for 0.5 mM P2T obtained by atomic adsorption spectroscopy measurements.

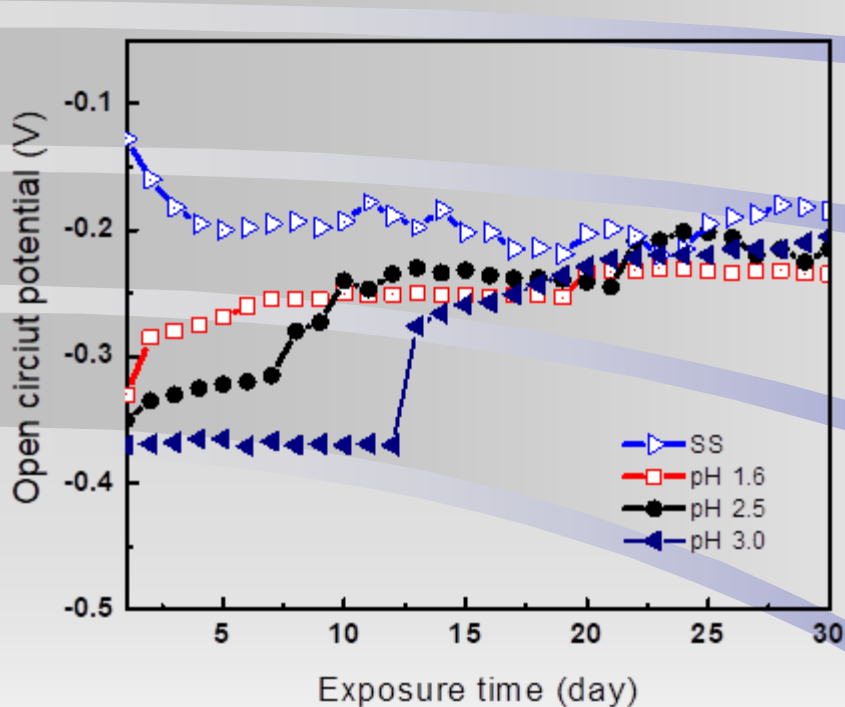


**Figure 3.** Copper and Zinc concentrations after an immersion time of 48 h in 0.5 M  $\text{H}_2\text{SO}_4$ .

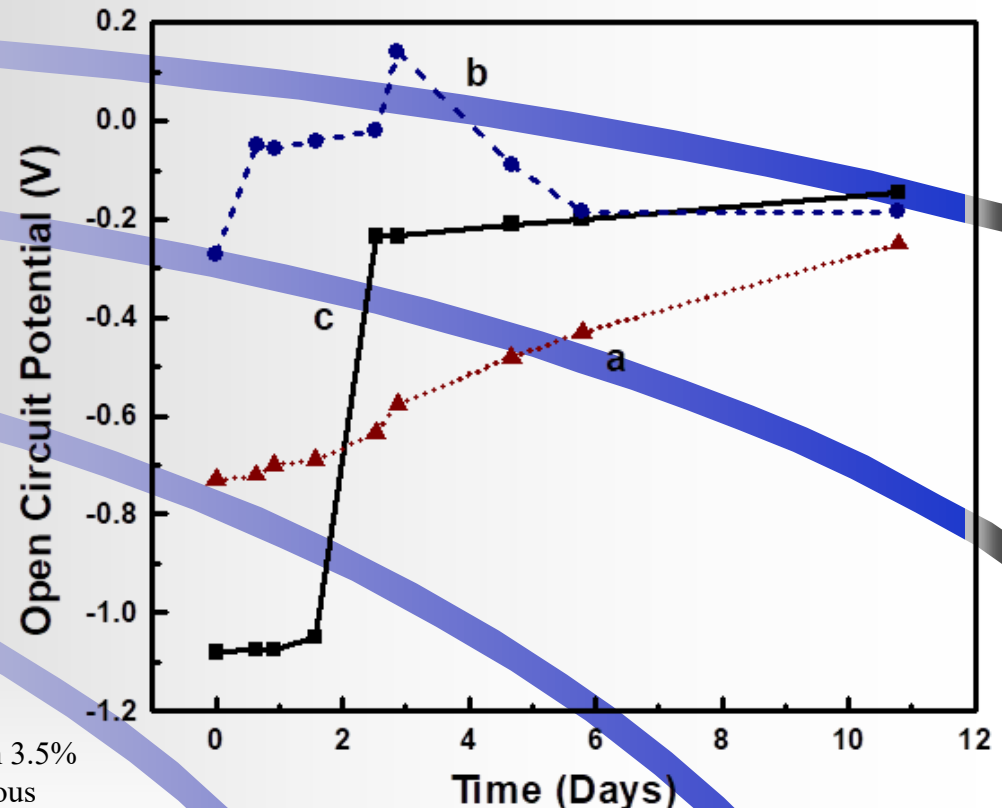
# Electrochemical Measurements for Corrosion

## Open Circuit Potential Studies

Monitor OCP versus time in corroding solutions.



**Figure 6.** Open circuit potential (OCP) versus immersion time in 3.5% NaCl for nickel-layered silicate films electrodeposited from various pHs (1.6, 2.5, 3.0). Values are an average of three runs with a standard deviation of  $\pm 0.02$ .

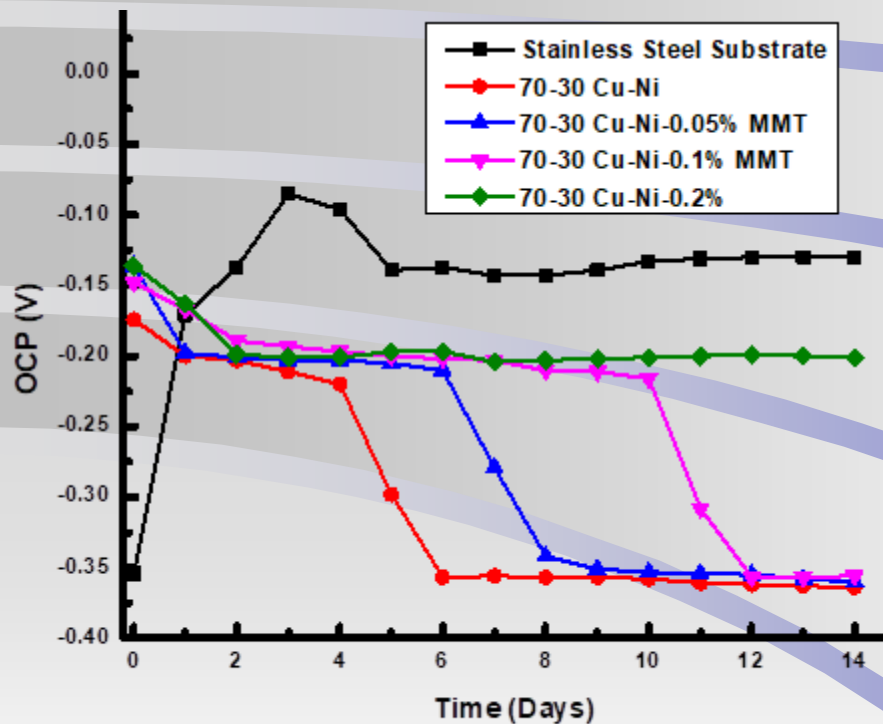


**Figure 8.** OCP submersion studies in 3.5% NaCl. (a) zinc-nickel  $\gamma$ -phase coating, (b) nickel coating and (c) zinc coating.

# Electrochemical Measurements for Corrosion

## Open Circuit Potential Studies

Monitor OCP versus time in corroding solutions.



**Fig. 6.** Plot of the immersion test for the 70-30 Cu-Ni coatings with and without MMT measured by OCP vs. time for 2 weeks in a 3.5% NaCl solution.

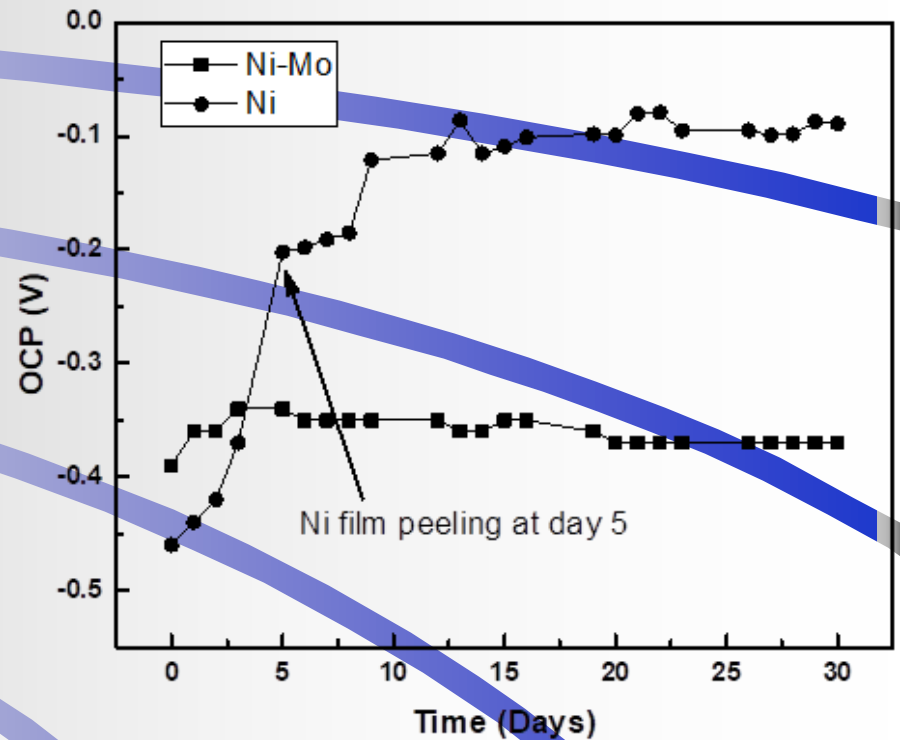


Figure 6: OCP Studies of the nickel-molybdenum coating over 30 days of immersion in 3.5 % NaCl solution.

# Electrochemical Measurements for Corrosion

## Open Circuit Potential Studies

Don't forget the pictures!

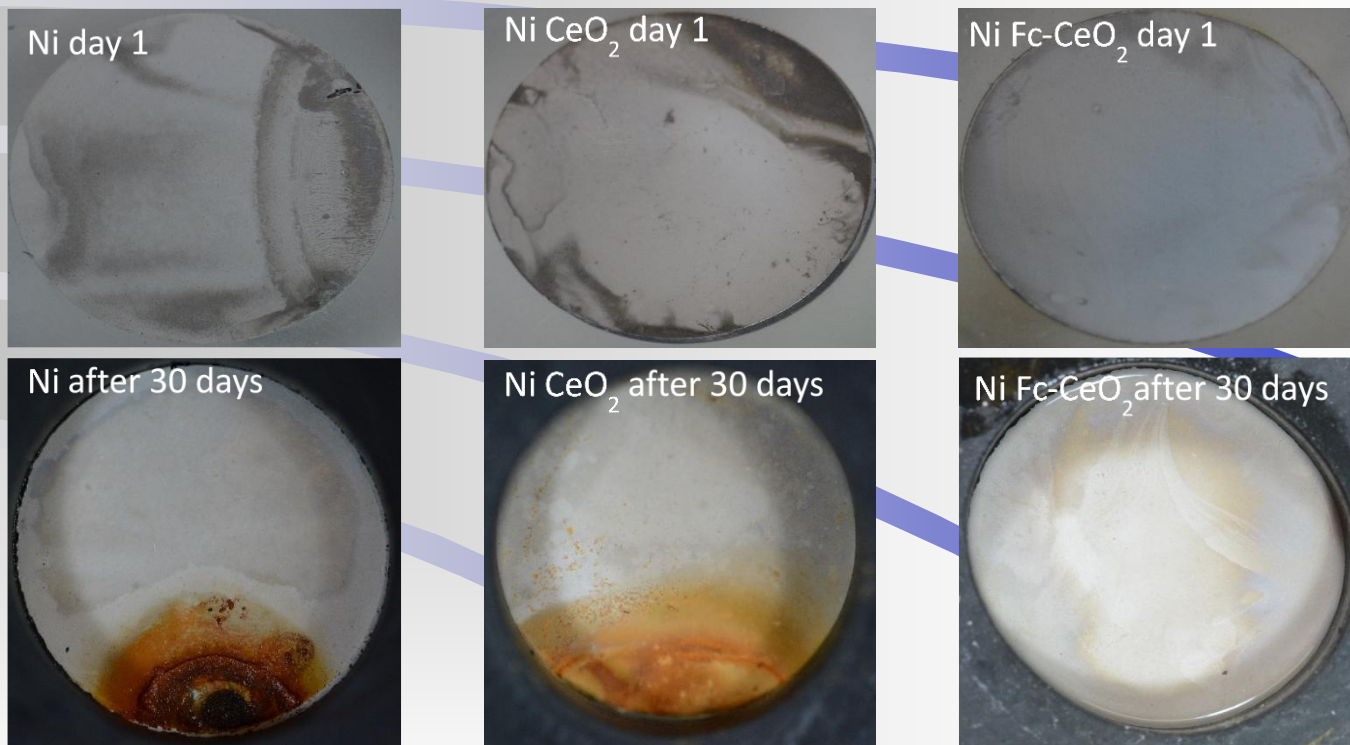
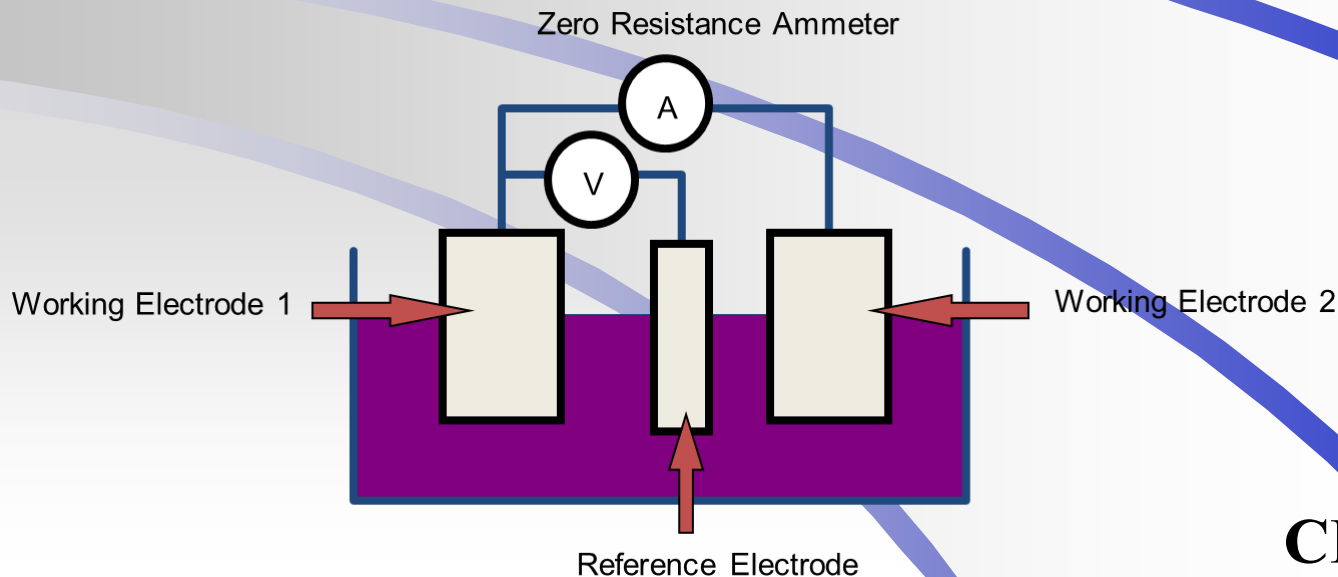


Figure S11. Photographs of pure Ni, Ni CeO<sub>2</sub>, and Ni Fc-CeO<sub>2</sub> coatings before and after 30 days of immersion in 3.5% NaCl.

# Electrochemical Measurements for Corrosion

## Electrochemical Noise (ECN)

- ECN measures the current/voltage response between two (largely) identical electrodes.
- The two electrodes are coupled together (short circuited together) through a zero resistance ammeter (ZRA).
- The random fluctuations of current is measure by the ZRA.
- At the same time the random fluctuations in voltage noise at the coupled electrodes is measured with respect to a reference electrode.



# Electrochemical Measurements for Corrosion

## Electrochemical Noise (ECN)

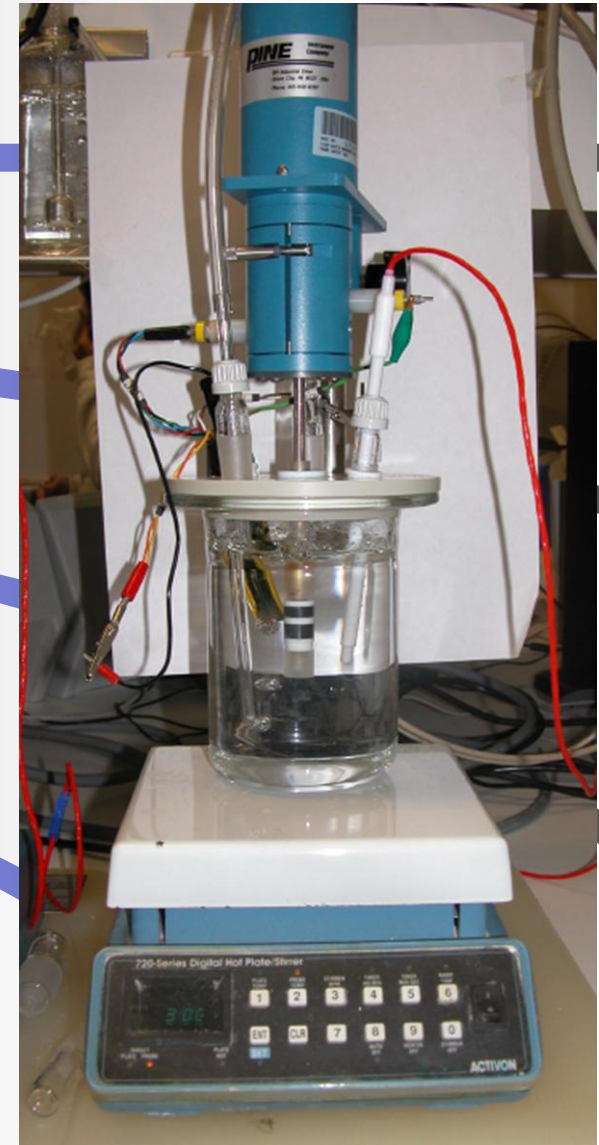
- Noise measurements can be used to evaluate the resistance (in this case noise resistance  $R_n$ ) of a material to its general, homogeneous corrosion in a given environment.
- Also hope to gain insight into the mechanisms (pitting, crevice, stress corrosion cracking, intergranular corrosion, etc.) governing this local corrosion.
- So far this hope has not been completely realized, but some progress has been made, and the method has been used for corrosion monitoring.
- Thus, EN is most commonly utilized in combination with other techniques such as LPR and EIS.

# Electrochemical Measurements for Corrosion

## Electrochemical Noise (ECN)

Can use Rotating dual cylinder electrode (RDCE) for measurements

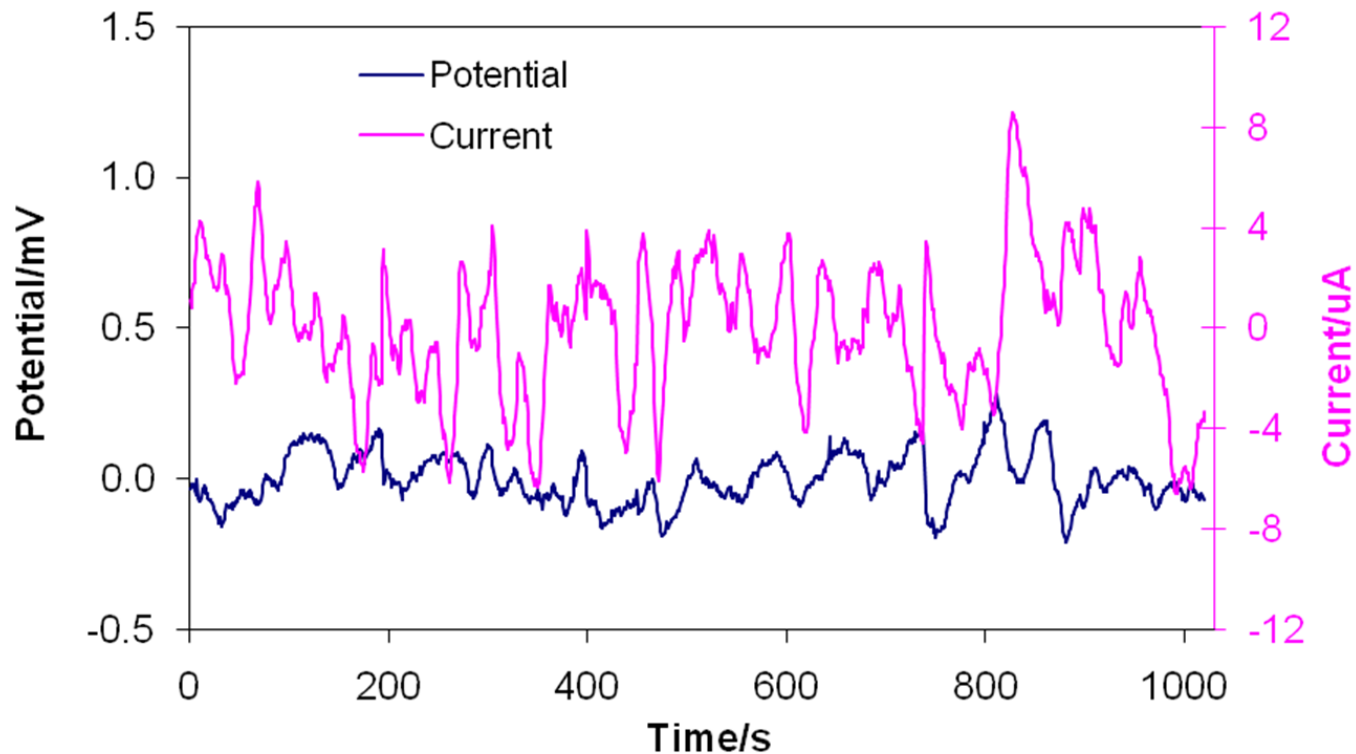
- Standard electrochemical cell with reference, auxiliary and RDCE
- The RDCE is useful for performing ECN Measurements
- ECN uses identical electrodes. In the example shown the electrode areas are not the same since this RDCE was used to investigate preferential weld corrosion



# Electrochemical Measurements for Corrosion

## Electrochemical Noise (ECN)

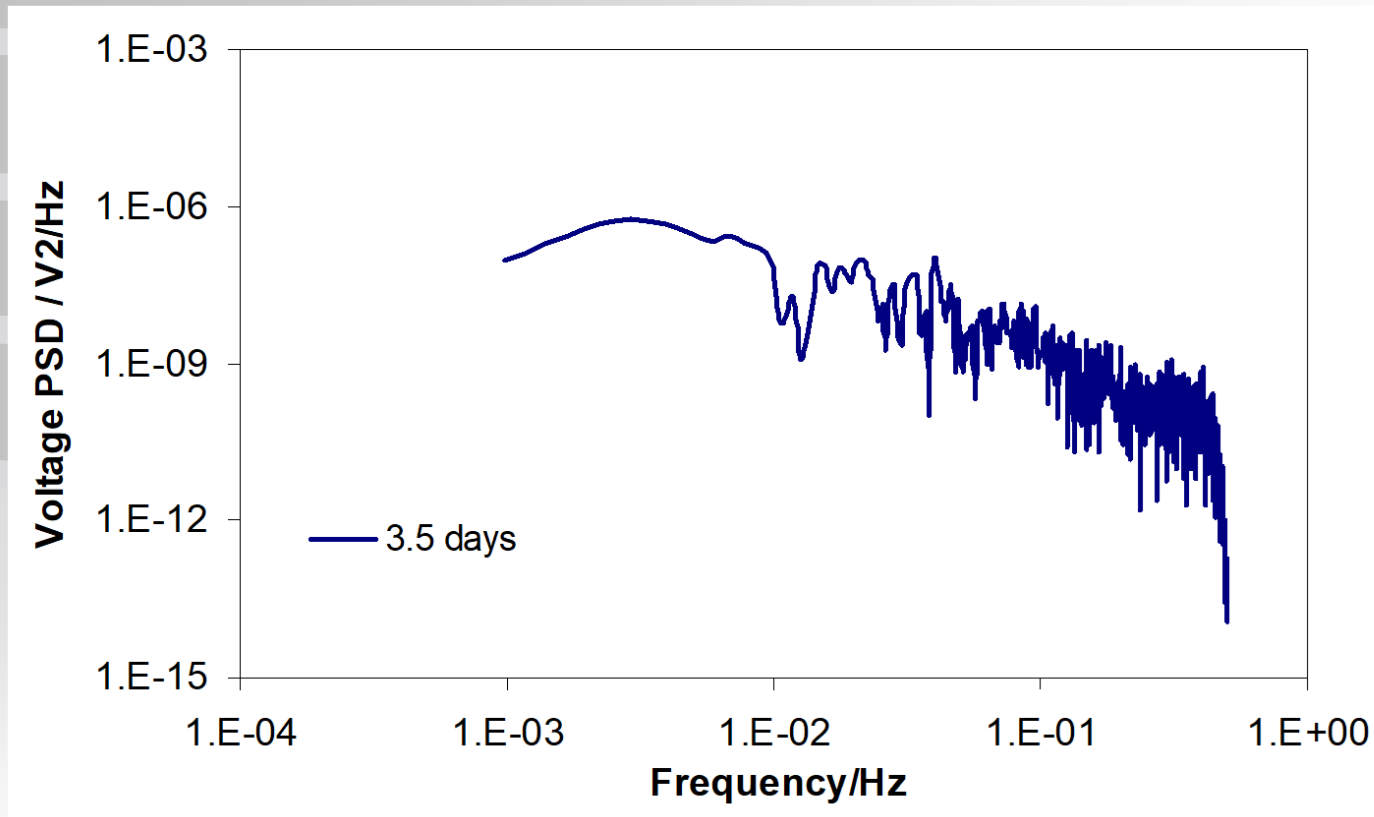
### Potential Noise and Current Noise



# Electrochemical Measurements for Corrosion

## Electrochemical Noise (ECN)

### Voltage Noise Power Spectral Density



# Electrochemical Measurements for Corrosion

## ASTM Techniques

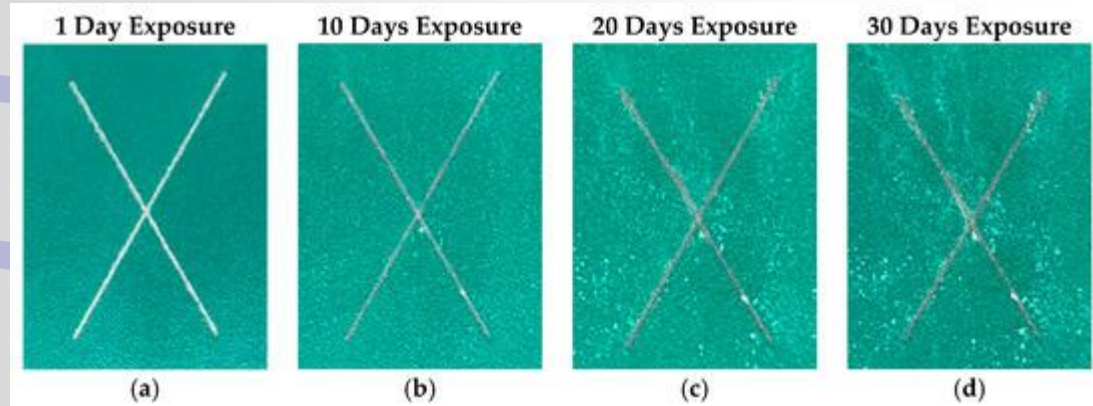
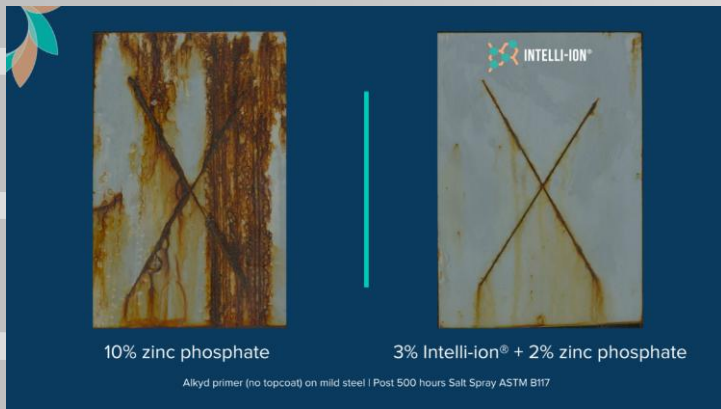
For non-conducting or almost non-conducting situations

ASTM D3359 is **a standard test methods for measuring adhesion by tape test**. This test assesses the adhesion of film coatings to metallic substrates by applying and removing pressure-sensitive tape over cuts made in the film. This test method is also known as the Cross Hatch test. Utilizing a tool to cut a right angle lattice pattern into the coating, penetrating all the way to the substrate. A quick pass/fail test can be accomplished through this method or a percentage of corrosion can be determined.

# Electrochemical Measurements for Corrosion

## ASTM Techniques

For non-conducting or almost non-conducting situations



Appearance of Cross-cut Area					
Percentage of Flaking	0%	<5%	<15%	<35%	<65%
Classification	<b>5B</b>	<b>4B</b>	<b>3B</b>	<b>2B</b>	<b>1B</b>

# Class Assignment

- Final – Dec 9<sup>th</sup> 8-10 am

