ANSWERS

MID TERM EXAM 2
Metals 497A
October 26, 2001

1a. What will happen to copper immersed in an acid open to air? Cu will corrode.

b. If the air is removed from the acid what will happen? Cu will be inert.

c. What reactions occur in (a)? Anodic: Cu → Cu^{2+} + 2e^{-}
   Cathodic: O_2 + 4H^+ + 4e^{-} → 2H_2O

d. Will the hydrogen evolution reaction (HER) occur in either (a) or (b)? no

e. Apply mixed potential theory to the cathodic and anodic reactions in (c) and show on your plot of the polarization curves, the value of the corrosion potential, E_{corr}, and of the corrosion rate, i_{corr}. Label the axes with units.

f. If the HER polarization curve is not already shown in the above plot, add it and use the plot in (e) to support your answer in (d). Cu oxidation will not displace hydrogen from the solution since the HER and Cu oxidation curves do not intersect.

2a. Using mixed potential theory illustrate how the corrosion rate of iron or steel increases as the pH becomes more acidic (assume the HER is the only cathodic reaction).
   Label the axes and give units.

b. In your plot in (a), did the anodic or cathodic curve change with pH? cathodic
b. On a semi-log plot of \( i \) and \( E \), what part of the polarization curve is the Tafel region? \( \text{the straight line sloped region of the curve.} \)

c. What process controls the rate of the reaction in the Tafel region? \( \text{the electron transfer reaction (for the processes considered in closed).} \)

d. Describe the process that controls the rate of reaction in the limiting current region of the oxygen reduction reaction, and name the species involved in this step:
\( \text{The diffusion of oxygen to the metal surface.} \)

e. Show the concentration profile for the process in (d) in a plot of concentration vrs. distance from the corroding sample, and show a second plot for an increased rate of stirring of the electrolyte. Label the axes.
\[
\begin{align*}
V &= \text{velocity} \\
V_2 &= V_1
\end{align*}
\]

f. Which equation or whose law can be used to calculate the rate of the process in (e)? \( \text{Fick's 1st Law: } i_{\text{lim}} = DnFCyS \)

g. What property is needed besides the concentration profile to calculate the rate using the equation in (f)? \( \text{the diffusivity of oxygen in the electrolyte} \)

h. The resistance of a corrosion reaction, \( R_p \), is determined by the resistance of both the anodic and cathodic reactions. Add the polarization curve of the cathodic reaction to your plot in (a) and then draw the measured curve in the region of the corrosion potential. How would you obtain the value of \( R_p \) from the measured curve? \( R_p = \text{the inverse slope of the measured curve at zero current (Ecorr) in the plot. Apply } \pm 10 \text{ mV at Ecorr and measure } \Delta i: R_p = \frac{\Delta E}{\Delta i} \text{ Ecorr as shown in the plot.} \)
c. What causes the polarization curve to shift along the E axis as the pH changes?

The change in the equilibrium potential of the HER with change in pH.

d. What form of corrosion protection could you apply using a battery to stop the corrosion process in your above plot in (a)?

Cathodic protection

Explain how it works:
The potential, $E$, of the iron is forced in the negative direction from $E_{corr}$ to a value more negative than the iron equilibrium potential.

e. Explain why the ammeter reads zero, whereas the corrosion rate, $i_{corr}$, in your plot in (a) is finite (i.e., $i_{corr} > 0$): At the corrosion potential, $E_{corr}$, the two reactions (A and C) occur at the same rate on the metal surface. Thus, there are no excess $e^-$ available to pass through an ammeter in an external circuit.

f. For the corrosion reaction in (a) occurring at pH 2, show on a Pourbaix (E vrs. pH) diagram the region where the corrosion potential, $E_{corr}$, will lie.

3a. Illustrate on a rectangular plot of anodic current density, $i$, and potential, $E$, how the resistance, $R$, of an electrode reaction decreases as the current increases. Label the axes and give units to the axes and to $R$. Label the equilibrium potential. $R_e (\text{ohm cm}^2)$