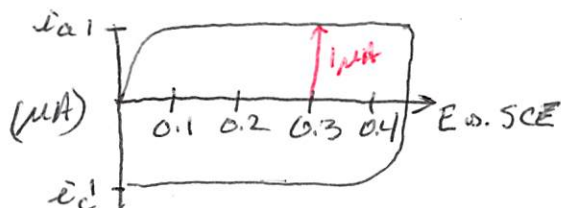


Name Answer Key

CEM 837
Quiz 3
Spring 2016

$$i = \frac{E}{R_s} \exp\left(\frac{-t}{R_s C_{dl}}\right) \quad \frac{\partial Q}{\partial t} = C \left(\frac{\partial E}{\partial t}\right) = i \quad i_{ch} = A C_{dl} \nu \quad i_{m,j} = |z_j| F A u_j C_j \frac{\partial \phi}{\partial x} \quad t_j = \frac{i_j}{i_{m,tot}} = \frac{|z_j| u_j C_j}{\sum_k |z_k| u_k C_k}$$

1 (3 pts). For the following current-voltage curve, what is the C_{dl} ($\mu\text{F cm}^{-2}$) at 0.3 V. The curve was recorded at a scan rate of 100 mV s^{-1} using an electrode of 1 cm^2 area. The electrolyte was 1 M KCl . $F = C \text{ V}^{-1}$



$$\begin{aligned} i_{ch} &= A C_{dl} \nu \\ C_{dl} &= \frac{i_{ch}}{A \nu} = \frac{(1 \times 10^{-6} \text{ A})}{(1 \text{ cm}^2)(0.1 \text{ V/s})} \\ &= 1.0 \times 10^{-5} \frac{\text{A} \cdot \text{s}}{\text{cm}^2 \text{V}} \quad \text{A} \cdot \text{s} = \text{C} \\ &= 1.0 \times 10^{-5} \frac{\text{F}}{\text{cm}^2} \quad \frac{\text{C}}{\text{V}} = \text{F} \\ &= 10 \mu\text{F/cm}^2 \quad \leftarrow \text{SO} \end{aligned}$$

2 (4 pts). Applying a potential to an electrode causes a corresponding current to flow that is associated with charging up the electrode double layer. This double layer must form before meaningful faradaic electron transfer can occur. How much current would have to flow initially (100 msec time point) in response to a rapid potential change? Assume the measurement was performed using a working electrode with a 1 cm^2 area, a solution resistance of 20 ohm , a double layer capacitance of $25 \mu\text{F cm}^{-2}$ and a potential step from 0 to $+1 \text{ V}$. 1 μsec

$$i = \frac{1 \text{ V}}{20 \text{ V} \cdot \text{s}} \exp\left(\frac{-100 \times 10^{-3} \text{ s}}{(20 \text{ V} \cdot \text{s}) \left(\frac{25 \times 10^{-6} \text{ F}}{\text{cm}^2}\right) (1 \text{ cm}^2)}\right) = (5.0 \times 10^{-2} \frac{\text{C}}{\text{s}}) \exp(-3.8 \times 10^{-8})$$

$$\begin{aligned} A &= \frac{C}{s} \quad C = FV \\ i_{ch} &= \left(\frac{1 \text{ V}}{20 \text{ V} \cdot \text{s}}\right) \exp\left(\frac{-1 \times 10^{-6} \text{ s}}{(20 \text{ V} \cdot \text{s}) \left(\frac{25 \times 10^{-6} \text{ F}}{\text{cm}^2}\right) (1 \text{ cm}^2)}\right) \\ &= (5.0 \times 10^{-2} \frac{\text{C}}{\text{s}}) (\sim 1) = 0.05 \text{ A} \\ &= 50 \text{ mA} \end{aligned}$$

a rather large current is forced to flow initially with a rapid potential step. Current decays to 0 as "capacitor" interface is fully charged.

3 (3 pts). In corrosion processes, there is always an anodic and cathodic reaction occurring at two different sites on the metal. Explain how increasing or decreasing the rate of dissolved O_2 transport to the surface will affect the rate of corrosion.

Assume that a current-potential curve was recorded for a corroding metal in aerated 1 M KCl. The cathodic current-potential curve revealed a diffusion limited current of $100 \mu A cm^{-2}$ at $-0.8 V$ vs. SCE due to transport of O_2 to the metal surface (no convection). If the measurement was made in much lower supporting electrolyte concentration, how much would the limiting current increase due to migration of O_2 to the surface? Assume $u(O_2) = 7.91 \times 10^8 m^2 s^{-1} V^{-1}$, $F = 96,500 C mol^{-1}$, $A = 1 cm^2$, $C = 2 mM$ and $\frac{\partial \phi}{\partial x} = -0.8 V$.

For a corroding metal, there is an oxidation reaction (metal oxidation) and a reduction reaction happening simultaneously. The reduction reaction consumes e^- 's generated by the corrosion reaction. O_2 is a good acceptor of e^- 's. The rate of the oxidation and reduction reactions are equal for the metal. Changing the flux of O_2 to the surface by either reducing the solution concentration (deaerating) or increasing the solution concentration (aerating), $J_{O_2} = -D_{O_2} \left(\frac{\partial c}{\partial x} \right)_{x=0}$, will decrease or increase the rate of corrosion, respectively.

If the rate of the cathodic reaction is increased, there must be a corresponding increase in the anodic reaction rate (i.e., the corrosion rate!)

$$i_{m, O_2} = \phi \text{ because } z=0.$$