CH 117 PS4
Solutions

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Comments and points from KMP 2017

Problem 1

20 pts **A)** The first thing to do here is to understand the possible structures of 7-HCFPA. In the linear structure—Fe-Pt-Fe-Pt-Fe-Pt-Fe—we have two (μ-CN)$_1$Fe and two (μ-CN)$_2$Fe. In the only possible branched structure, remembering that each Pt has exactly **two** CN ligands—Fe-Pt-Fe-(Pt-Fe)$_2$—we have three (μ-CN)$_1$Fe and one (μ-CN)$_3$Fe. Furthermore, we notice that the linear 7-HCFPA is the only possible structure having only (μ-CN)$_1$Fe and (μ-CN)$_2$Fe and possessing an equal number of (μ-CN)$_1$Fe and (μ-CN)$_2$Fe.

With this analysis complete, we look at the CV. For this particular CV, it would be difficult to use the cut-and-weigh procedure, so we can use the peak height as a stand-in for the concentration (this assumes a similar mechanism in the two peaks). Measuring the peak heights, we find them to be approximately the same at 0.55 and 0.85 V vs. SCE. This implies that we have an equal number of (μ-CN)$_1$Fe and (μ-CN)$_2$Fe. 4 pts We assume that the experiment was carried out to check for higher numbers of bridging cyanides and found none. Thus, from our analysis above, this data can only be consistent with the linear 7-HCFPA structure. 4 pts

B) First we note that only (μ-CN)$_1$Fe, (μ-CN)$_2$Fe, and (μ-CN)$_3$Fe are present. Again, measuring the peak heights, we find a ratio of about 1:2:2 for (μ-CN)$_1$Fe:(μ-CN)$_2$Fe:(μ-CN)$_3$Fe. 4 pts There are probably a lot of structures that could fulfill this ratio, but we can eliminate some broadly. First, the presence of $(\mu\text{-CN})_3\text{Fe}$ indicates that we can't have a linear structure. Second, the small number of terminal irons indicates that we must have some cycles in our system. In the absence of cycles we always have $\#(\mu\text{-CN})_1\text{Fe} = 2 + \#(\mu\text{-CN})_3\text{Fe}$ for any branched structure. Thus, we can't have twice as many $(\mu\text{-CN})_3\text{Fe}$ without having some cycles, and the structure is not branched. That leaves either the two dimensional sheet or the three dimensional network. We can easily draw two dimensional structures that satisfy the ratio above, and one imagines that a three dimensional network would require Fe atoms with four or more bridging cyanides. If we also note that the peak separation on the CV is very small, the polymer may be surface bound. Thus, we suggest that the structure is a **two dimensional sheet**.

4 pts

C) Beginning with an excess of 3-HCFPA in presence of $[\text{Pt(NH}_3)_4]^{2+}$, we apply a potential around 0.55 V vs. SCE, which will oxidize only the terminal Fe in an extended structure and enable the formation of linear polymers having high n.

4 pts

Problem 2

60 pts

A) Peak B is due to surface bound $[\text{NiFe(CN)}_6]^{2-/-}$. The small peak to peak separation in scan B and the high symmetry of the peaks in B both suggest a surface bound species rather than one in solutions. Furthermore, comparing this scan with scan D (a bare Ni electrode in supporting electrolyte), we see that the wave must be due to the presence of the $[\text{NiFe(CN)}_6]^{2-/-}$.

4 pts for reasoning, 4 pts for answer

B) We could calculate the coverage either by integrating the area under the curve and assuming 100% faradaic efficiency, or by using the peak current with Bard equation 14.3.12 and assuming facile kinetics. If we use the peak current, then the relevant relation is:

$$i_p = \frac{n^2F^2}{4RT}\omega A\Gamma_R$$

Hint was given to do this

The area of the peak has units of A × V = J/s, which can be converted to the total charge passed by dividing by the scan rate. With the total charge passed, we can calculate the coverage from:

$$Q = nFA\Gamma_R$$

In either case, a value of 4×10^{-7} mol/cm^2 is expected.

8 pts, 4 each for answer and units

C) There could be more than one symmetry defined here—the difference between $i_{p,c}$ and $i_{p,a}$ or the asymmetry within each peak. The peaks in scan B are only symmetric because they are due to a surface confined species with reversible, facile kinetics. Thus, the asymmetry in scan A is due to the quasi-reversible kinetics of the hydrazine oxidation as well as the diffusional nature of the reaction since it is hydrazine in solution reacting.

4 pts

D) We can immediately rule out mechanism (a) because of C in the left plot. We can clearly see that there must be some effect of the $[\mathrm{NiFe(CN)_6}]^{2-/-}$ lattice, so that hydrazine must not have to diffuse all the way to the Ni interface. In order to distinguish between the other two mechanisms, we can use the scan rate dependence and try to use the Nicholson and Shain diagnostics. We first note that the peak position of the anodic peak shifts with scan rate while the position of the cathodic peak remains fixed. This implies that the cathodic wave is due largely to reduction of the surface bound $[\mathrm{NiFe(CN)_6}]^{2-}$ and thus that the mechanism must be one of II, IV, or VIII. If we measure the peak currents and plot $i_{p,a}/\omega^{1/2}$ as a surrogate for the current function, we see that the current function is strongly decreasing with increasing scan rate (See below). This implies mechanism IV or VIII of the ones listed above. Examining these mechanisms, we see that IV is a fast pre-equilibrium followed by an irreversible charge transfer, which might correspond with intercalation of hydrazine into the $[\mathrm{NiFe(CN)_6}]^{2-/-}$ lattice. On the other hand VIII is the catalytic or mediated charge transfer mechanism. Finally, plotting $\Delta E_{p/2}/\Delta \log \omega$ gives somewhat mixed results. The shape is reminiscent of mechanism VIII, providing more evidence for the mediated charge transfer. From this data, it is likely that either (b) or (c) is correct.

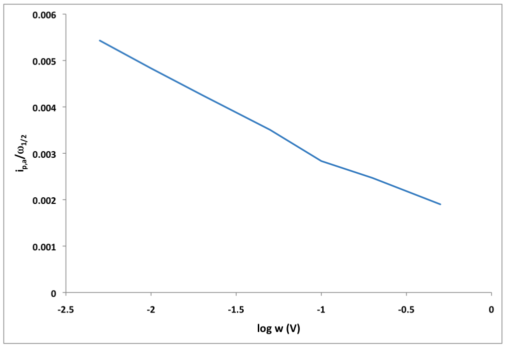
4 pts

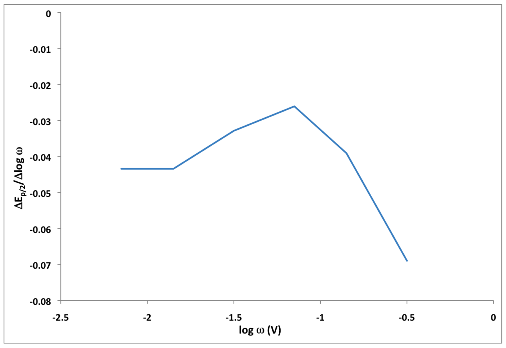
making the plot = 4 pts

narrowing down the options = 4 pts

extra credit item = 4 pts

4 pts for inconclusive result





E) In this problem we are changing the driving force by changing the cation. The driving force for the oxidation increases in the order $\mathrm{Na}^+ < \mathrm{Rb}^+ < \mathrm{Cs}^+$. In addition, we see that the peak current is decreasing with increasing driving force, indicating a decrease in the rate constant. Thus, a naive application of Marcus theory indicates that we are in the inverted region. However, it is more likely that the change in lattice constant changes the nature of the reaction.

4 pts

F) We see that the limiting current obtained is given by Bard, equation 9.3.33 (we flip the sign because Bocarsly is using a different convention than Bard—anodic currents are positive):

$$i_{l,a} = 0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R^*$$

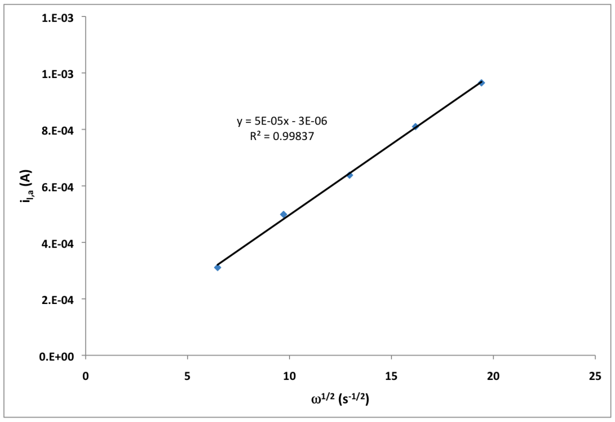
Where ν is the kinematic viscosity and is reported to have a value of approximately 0.01 cm^2/s (Bard page 337). Recalling that $\omega = 2\pi f$, we can plot $i_{l,a}$ vs. $\omega^{1/2}$ and use the slope to obtain the diffusion coefficient of hydrazine:

$$D_R = \left(\frac{\text{slope}}{0.62nFA\nu^{-1/6}C_R^*}\right)^{3/2}$$

Using the graph below, we calculate the diffusion coefficient to be 4.66×10^{-5} cm^2/s.

4 pts for the graph

4 pts for the answer



G) The peak in this panel is due to the oxidation of surface bound $[\mathrm{NiFe(CN)_6}]^-$. This is possible in the RDE experiment because surface bound material is not subject to the mass transport limitations imposed by bringing materials to the surface.

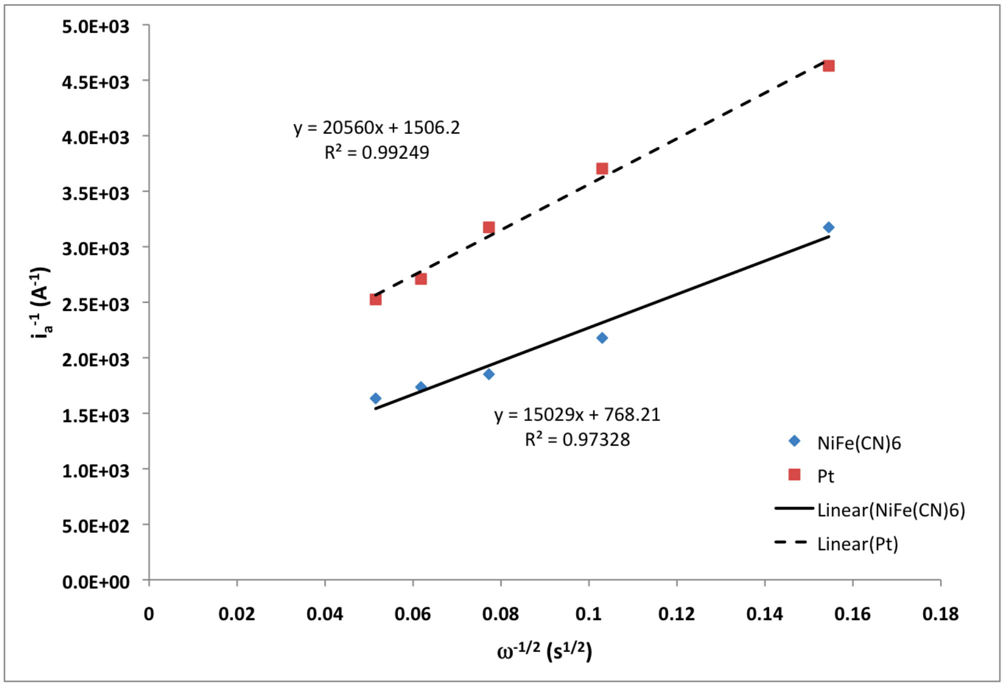
4 pts

H) We can calculate the kinetic current, i_K, using the Koutecky-Levich equation (Bard 9.3.39):

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{l,a}} = \frac{1}{i_K} + \frac{1}{0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R^*}$$

Therefore, we expect a plot of $1/i$ vs. $\omega^{-1/2}$ to be linear with intercept $1/i_K$. We expect i_K to be proportional to k_f which is highly voltage dependent, so the number measured will depend on the potential chosen. However, it is better to choose a potential in the sloping region of the curve as this is where the reaction kinetics are likely to manifest. In the limiting portion of the curve, there is no kinetic influence. We calculate the values of i at a potential of 0 V vs. SCE. Shown below is the Koutecky-Levich plot for both Ni and Pt at 0V (the Pt plot is for part I). From the intercept, we find that $i_K = 1.3$ mA at 0 V vs. SCE.

4 pts for the other K-L plot



I) To evaluate the kinetics, it would be ideal to calculate the value of k^0 for each electrode, but it will suffice just to examine i_K at a given potential. From the plot above, we can see that i_K for Pt is about 0.66 mA. Given that we know that the electrodes have the same area, we can see that the derivatized Ni has more facile kinetics and is therefore a better catalyst for hydrazine oxidation.

4 pts for some reasonable approach and answer

At high rotation rates, the plateau current is lower for the Ni/$[\mathrm{NiFe(CN)_6}]^{2-/-}$ electrode, but this is not necessarily an indication of kinetic limitations. In fact, the lower plateau currents at very high rotation rates are due to mass transport of hydrazine through the lattice. Therefore, this is further evidence that intercalation of hydrazine into the lattice is important for this process.

20 pts

Problem 3

We begin with the Cottrell equation;

$$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

Now, since the system is surface confined in a layer of thickness d, we can write:

$$dC_O^* = \Gamma^* \Longrightarrow C_O^* = \frac{\Gamma^*}{d}$$ 4 pts

Integrating the Cottrell equation with respect to t and plugging in for C_O^*, we obtain:

$$Q(t) = \frac{2nFAD_O^{1/2}\Gamma^* t^{1/2}}{\pi^{1/2}d}$$ 4 pts

Furthermore, we can calculate the total charge that would be consumed after reducing the entire layer, Q_T, as:

$$Q_T = nFA\Gamma^*$$ 4 pts

Taking the ratio $Q(t)/Q_T$, we find:

$$\frac{Q(t)}{Q_T} = \frac{2D_O^{1/2}t^{1/2}}{\pi^{1/2}d}$$ 4 pts

And therefore:

$$\left[\frac{Q(t)}{Q_T}\right]^2 = \left(\frac{4}{\pi}\right)\left(\frac{D_O}{d^2}\right)t$$ 4 pts