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3.53 ELECTROCHEMICAL PROCESSING OF MATERIALS

Test 1 April 12, 2001

USE OF *Bard & Faulkner* PERMITTED. NO NOTES ALLOWED.

1. (a) From the data given in Figure 3.4.5 in Bard & Faulkner (2nd ed.)[1] estimate i_o for the reduction of Mn(IV) to Mn(III) on platinum at 298 K in 7.5 M H_2SO_4 containing 0.353 M Mn(III) and 0.4 M Mn(IV). The platinum microelectrode is 0.8 mm in diameter.

40%

(b) Estimate the limiting current density for the reduction of Mn(IV) to Mn(III) on platinum at 298 K in 7.5 M H_2SO_4 containing 10^{-2} M Mn(III) and 10^{-3} M Mn(IV).

(c) Estimate the overpotential at which the current for the reduction of Mn(IV) to Mn(III) on platinum at 298 K in 7.5 M H_2SO_4 containing 10^{-2} M Mn(III) and 10^{-3} M Mn(IV) has a value of 3.53 i_o.

(d) Estimate the overpotential at which the current density for the oxidation of Mn(III) to Mn(IV) on platinum at 298 K in 7.5 M H_2SO_4 containing 10^{-2} M Mn(III) and 10^{-3} M Mn(IV) has a value 10^{-4} A/cm^2.

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[1] Figure 3.5.5 in B&F 1st edition.

2.   In a series of experiments involving the use of controlled step potential
     chronoamperometry, the following data were measured at a stationary planar
     microelectrode. At each potential, the current was recorded after an elapsed
     time, τ, of 3.53 seconds. The voltages are referenced against the NHE.

35%

E(V)	$i_{t=\tau}/i_d$
–0.361	0.1
–0.411	0.3
–0.436	0.7
–0.459	0.9

The overall reaction is $O + e \rightarrow R$. $C_O^* = 3.53$ mM, and initially there is no R
present in solution. From independent measurements $E^{\circ\prime}$ is known to have a
value of –0.22 V against the NHE. The reaction is totally irreversible.

(a) Estimate the charge transfer resistance, R_{ct}.

(b) *Without performing the numerical calculation*, explain how to estimate the
     mass transfer resistance, R_{mt}, from these data. Include the necessary equations
     in your explanation.

DATA:
electrode area, $A = 0.01$ cm^2
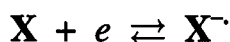diffusion coefficient of O, $D_O = 6.66 \times 10^{-5}$ cm^2 s^{-1}

3.   Solutions of **X** in an appropriate supporting electrolyte were studied by cyclic voltammetry.

25%

It is found that **X** can be oxidized at ≈ 0.6 V to form the radical cation, $\mathbf{X}^{+\cdot}$, according to

$$\mathbf{X} \rightleftarrows \mathbf{X}^{+\cdot} + e$$

and reduced at ≈ -1.4 V to form the radical anion, $\mathbf{X}^{-\cdot}$, according to

$$\mathbf{X} + e \rightleftarrows \mathbf{X}^{-\cdot}$$

All reaction products appear to be stable.

(a) On the same graph, sketch cyclic voltammograms for the following experiments. In each case the system begins from the same initial condition: only **X** and no reaction products present in solution. All scans start at –0.1 V and move first in a positive direction.

   (i)   Pt working electrode, scan rate = 10 mV/s, oxidation and reduction peaks appear reversible

   (ii) Pt WE, scan rate = 100 mV/s, oxidation peak appears reversible, reduction peak appears marginally sluggish (quasi reversible)

   (iii) vitreous carbon WE, scan rate = 10 mV/s, oxidation and reduction peaks appear highly irreversible

(b) Why should the choice of WE influence the kinetics of the electron transfer reaction when all reactants and products are soluble?