Model Solutions to 3.53 Problem Set 6

Problem 10.4 **(a).** The approach to this problem is outlined in the first edition of Electrochemical Methods, page 348-349. Consider the circuit in Figure 10.1.14 where R_Ω is in series with parallel components of C_d and the faradaic impedance, Z_f. The faradaic impedance is represented as a series RC circuit where the elements are R_s and C_s. If Z_f is isolated from R_Ω and C_d, then R_s and C_s can be determined. The trick is to note that for resistors in series, the total resistance is the sum of the resistances; for capacitors in parallel, the total capacitance is the sum of the capacitances. R_Ω and C_d can be eliminated by first considering a series circuit (to eliminate R_Ω) and then a parallel circuit (to eliminate C_d).

First, consider R_B which is composed of two components, R_Ω in series with the parallel element. As this is a series circuit, the measured resistance R_B can be expressed as $R_B = R_\Omega + R'_B$ where R'_B is the resistance of the parallel element. Thus, the solution resistance can be eliminated as

$$R'_B = R_B - R_\Omega \tag{1}$$

Second, this leaves a parallel circuit where C_d is in parallel with the faradaic impedance. The series values (R'_B and C_B) can be converted to parallel components following the equations developed in Problem 10.2 and outlined in the first edition on page 348. For $W = (\omega RC)^2 = (\omega R'_B C_B)^2$,

$$R_p = R\left[\frac{W+1}{W}\right] = R'_B\left[\frac{W+1}{W}\right] \tag{2}$$

$$C_p = \frac{C}{W+1} = \frac{C_B}{W+1} \tag{3}$$

Then, the double layer capacitance is eliminated as

$$C'_p = C_p - C_d \tag{4}$$

Third, the faradaic impedance remains in a parallel arrangement. It remains to convert the parallel form to the series form. Equations are provided in Problem 10.2 and on page 348 in the first edition. For $W_p = (\omega R_p C'_p)^2$,

$$R_s = \frac{R_p}{1+W_p} \tag{5}$$

$$C_s = C'_p\frac{1+W_p}{W_p} \tag{6}$$

Finally, the phase angle is calculated from equation (10.3.9). Note that radians are converted to degrees by multiplying by $180°/\pi$.

$$\phi = \tan^{-1}\left[\frac{1}{\omega R_s C_s}\right] = \arctan\left[\frac{1}{\omega R_s C_s}\right] \tag{10.3.9}$$

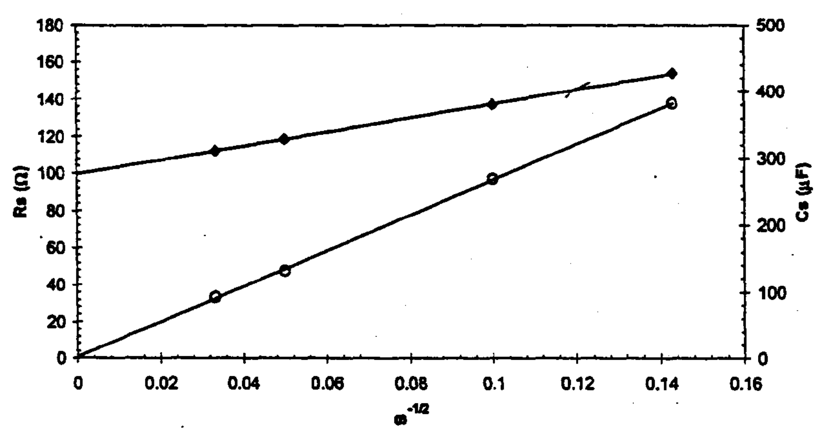
Values and the corresponding equations are tabulated on the next page. $R_s = 10\ \Omega$; $C_d = 20.0\ \mu F$.

		eqn.	Freq. (Hz)			
			49	100	400	900
R_B	(Ω)		146.1	121.6	63.3	30.2
C_B	(μF)		290.8	158.6	41.4	25.6
$R'_B = R_B - R_\Omega$	(Ω)	(1)	136.1	111.6	53.3	20.2
$W = (\omega R'_B C_B)^2$			3.761	3.133	0.779	0.217
R_p	(Ω)	(2)	172.3	147.2	121.7	113.5
C_p	(μF)	(3)	61.1	38.4	23.3	21.0
$C'_p = C_p - Cd$	(μF)	(4)	41.1	18.4	3.3	1.0
$W_p = (\omega R_p C'_p)^2$			0.120	0.0732	0.0254	0.0113
R_s	(Ω)	(5)	153.8	137.2	118.7	112.2
C_s	(μF)	(6)	382.6	269.5	132.3	93.1
$[\omega R_s C_s]^{-1}$			0.347	0.271	0.159	0.106
ϕ	(rad)	(10.3.9)	0.334	0.264	0.158	0.106
ϕ	(deg)	(10.3.9)	19.1	15.1	9.05	6.07

(b). Plots of R_s and C_s versus $\omega^{-1/2}$ will be linear and yield R_{ct} and σ.

$$R_s = R_{ct} + \frac{\sigma}{\omega^{1/2}} \tag{10.2.25}$$

$$C_s = \frac{1}{\sigma\omega^{1/2}} \tag{10.2.26}$$



Markers: R_s (♦) and C_s (○)

Relevant definitions are provided by equations (10.3.2), (3.4.6), and (10.3.10).

$$R_{ct} = \frac{RT}{Fi_0} \tag{10.3.2}$$

$$i_0 = nFAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha} \tag{3.4.6}$$

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}} \left[\frac{1}{\sqrt{D_O}C_O^*} + \frac{1}{\sqrt{D_R}C_R^*} \right] \tag{10.3.10}$$

Regression analysis yields $R_s = 99.6 + 378/\omega^{1/2} = R_{ct} + \sigma/\omega^{1/2}$ and $C_s(F) = 2.66 \times 10^{-3}/\omega^{1/2} = 1/\sigma\omega^{1/2}$. Thus, $R_{ct} = 99.6\ \Omega$ and $\sigma = 378$.

Equation (10.3.2) yields

$$i_0 = \frac{RT}{FR_{ct}} = \frac{0.02569\ V}{99.6\ \Omega} = 2.58 \times 10^{-4}\ A \tag{7}$$

It is given that $n = 1$, $A = 1\ cm^2$, and $C_O^* = C_R^* = C^* = 1.00 \times 10^{-6}\ mol/cm^3$, such that from equation (3.4.6),

$$\begin{aligned} k^0 &= \frac{i_0}{nFAC^*} \\ &= \frac{2.58 \times 10^{-4}\ A}{96485\ C/mol \times 1\ cm^2 \times 1.00 \times 10^{-6}\ mol/cm^3} = 2.67 \times 10^{-3}\ cm/s \end{aligned} \tag{8}$$

From equation (10.3.10),

$$\begin{aligned} \sqrt{D} &= \frac{\sqrt{2}RT}{\sigma n^2F^2AC^*} \\ &= \frac{\sqrt{2} \times 0.02569\ V}{378\ \Omega/s^{1/2} \times 96485\ C/mol \times 1\ cm^2 \times 1.00 \times 10^{-6}\ mol/cm^3} \\ &= 9.96 \times 10^{-4}\ cm/s^{1/2} \\ D &= 9.92 \times 10^{-7}\ cm^2/s \end{aligned} \tag{9}$$