Question 1a

Cyclic Voltammograms at Different Scan Rates

Working Electrode Potential vs. Time
**Question 1b**

I measured the $i_{pc}$ and plotted below.

\[ n = 0.30 \quad \text{and} \quad i_{pc} = 2.68 \times 10^{-6} \text{A} \]

Randles-ScoviK

So slope = $2.68 \times 10^{-6} \text{A} \cdot \text{V}^{-1/2}$

Anode: $1.467 \times 10^{-3} \text{C} \cdot \text{cm} \cdot \text{mol}^{-1} \cdot \text{s}^{-1/2}$

Cathode: $1.408 \times 10^{-3} \text{C} \cdot \text{cm} \cdot \text{mol}^{-1} \cdot \text{s}^{-1/2}$

\[ D = 5.105 \times 10^{-6} \text{cm}^2 \text{s}^{-1} \]

\[ D = 4.698 \times 10^{-6} \text{cm}^2 \text{s}^{-1} \]

**Ipc vs v^{1/2}**

\[ y = 1.46735E-03x \]

\[ R^2 = 9.92396E-01 \]

\[ y = 1.40766E-03x \]

\[ R^2 = 9.90683E-01 \]
Question 1c

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

The above equation has been taken from the lecture notes, and describes flux of atoms towards the surface if an electrode in the x direction. The first term is diffusion, the second is drift/migration, and the third is convection. Diffusion is the dependent on the diffusion coefficient and the concentration gradient that occurs as reactions are taking place at the electrode surface. Migration occurs when charged species are pushed a certain direction based on the electric field created in the cell. This can be ignored in most cases if a mM-M concentration of supporting electrolyte is used. Convection is dependent on the concentration of the solution, and the velocity profile of the solution.

If we have a low concentration and don’t stir, then the flux will be diffusion limited. This is demonstrated when there are precise peaks on a cyclic voltammogram, where the peaks represent the optimal voltage at which the kinetics of the reaction can best overcome the concentration gradient at the electrode surface. This is considered to be non-steady-state diffusion, as the location of the boundary layer can change over time.

If we have a large concentration and stir quickly, the convection term will dominate the flux. This is demonstrated by jagged lines at constant currents past the reduction potential for a given redox event. This is due to the fact that, while there is a concentration gradient limiting the amount of redox species near the electrode, the location of the boundary layer is unchanged throughout the experiment, as stirring will replenish unreacted species and remove reacted species very close to the surface at a constant rate. This means, while the concentration gradient at the surface of the electrode is still controlling the rate of the reaction, the convection of the system is keeping the boundary layer a fixed length. **Therefore, the concentration at the surface is dependent on diffusion, but the concentration outside the boundary layer is dependent on convection.**

Gaurav’s Comment : Stirring results in a well-defined, time invariant (or something meaning steady state) boundary layer at a short distance from working electrode. (Optional : This leads to removal of hysteretic behavior) : 2 points

Flux outside boundary layer: J (convection) 1 point
Flux inside boundary layer : J (diffusion) 1 point
**Question 2a**

We know: Roughness factor = \( \frac{\text{Capac. Mno}_2}{\text{Capac. FTO}} \)

To determine each capacitance, we must integrate the cathodic and anodic sweep of the 2nd CV and average the two. Then, dividing this quantity by the scan rate will give us the charge passed. Dividing the charge passed in a non-faradaic region by the potential range tells us the capacitances. We can also compare \( \frac{Q_{MnO_2\text{ LiClO}_4}}{Q_{MnO_2\text{ TBA}}} \) to find the intercalation charge storage.

<table>
<thead>
<tr>
<th>FTO in TBA</th>
<th>M\text{no}_2 \text{ in TBA}</th>
<th>M\text{no}_2 \text{ in LiClO}_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>anode</td>
<td>cathode</td>
<td>anode</td>
</tr>
<tr>
<td>2.74 x 10^{-6} mA-V</td>
<td>1.77 x 10^{-6} mA-V</td>
<td>4.89 x 10^{-3} mA-V</td>
</tr>
<tr>
<td>cathode</td>
<td>anode</td>
<td>cathode</td>
</tr>
<tr>
<td>1.77 x 10^{-6} mA-V</td>
<td>2.91 x 10^{-4} mA-V</td>
<td>1.98 x 10^{-2} mA-V</td>
</tr>
<tr>
<td>avg</td>
<td>2.257 x 10^{-6} mA-V</td>
<td>2.09 x 10^{-4} mA-V</td>
</tr>
<tr>
<td></td>
<td>2.09 x 10^{-4} mA-V</td>
<td>avg = 3.435 x 10^{-3} mA-V</td>
</tr>
</tbody>
</table>

\[
Q_{\text{FTO}} = \frac{2.257 \times 10^{-6} \text{mA-V}}{0.010 \times \frac{1}{8}} = 2.257 \times 10^{-4} \text{mC}
\]

\[
Q_{\text{MnO}_2 \text{TBA}} = \frac{2.09 \times 10^{-4} \text{mA-V}}{0.010 \times \frac{1}{8}} = 2.09 \times 10^{-3} \text{mC}
\]

\[
Q_{\text{MnO}_2 \text{ LiClO}_4} = \frac{3.435 \times 10^{-3} \text{mA-V}}{0.010 \times \frac{1}{8}} = 3.435 \times 10^{-1} \text{mC}
\]

\[
Q_{\text{Li}^+} = 2.09 \times 10^{-2} \text{mC} - 3.435 \times 10^{-1} \text{mC} = 0.93 \text{ mC} = \text{Fraction of charge storage from Li}^+ \text{ int.}
\]
Question 2b  
Assuming $\text{Mn(OH)}_4^\text{-} \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + 2\text{e}^-$

$\text{Mn}^{2+} \rightarrow \text{MnO}_2$

$\text{Mn}^{2+} + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^-$

We know: Faradaic Efficiency $= \frac{Q_{\text{exp}}}{Q_{\text{theo}}}$

$Q_{\text{theo}}$: I integrated the CA data

\[ Q_{\text{theo}} = 80.1981 \text{ mC s}^{-1} = 8.02 \times 10^{-3} \text{ C} \]

\[ Q_{\text{exp}} = n \times F \times \text{mol MnO}_2 = 2 \times 96485.3 \text{ C} \times \frac{10^{-7} \text{ mol}}{\text{min}} \times \frac{3 \text{ min}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{86.9 \text{ g}} \]

From eq

\[ Q_{\text{exp}} = 6.66 \times 10^{-4} \text{ C} \]

Faradaic Efficiency $= \frac{6.66 \times 10^{-4} \text{ C}}{8.02 \times 10^{-3} \text{ C}} = 0.0083$
Capac FTO = \[
\frac{2.257 \times 10^{-4} \text{ mF}}{0.3 \text{ V}} = 7.5 \times 10^{-4} \text{ mF}
\]

Capac \text{ MnO}_2 = \[
\frac{2.09 \times 10^{-3} \text{ mF}}{0.3 \text{ V}} = 6.967 \times 10^{-2} \text{ mF}
\]

Roughness = \[
\frac{6.967 \times 10^{-2} \text{ mF}}{7.5 \times 10^{-4} \text{ mF}} = 92.6 = \text{ Roughness factor}
\]

You could also just take the ratio of the integrated areas from the CV's because we used the same scan rate and potential window.
I integrated this plot to get my $Q_{\text{theo}}$.

\begin{center}
\textbf{Chronoamperogram of MnO2 Deposition}
\end{center}

**Question 2c**

While the pH of the solution is 11, the pH at the surface of the electrode may not be. During electrodeposition, the bulk pH is not as important at the pH near the electrode surface. If the local pH is somewhere lower than 11, the soluble Si ionic species may turn into an insoluble SiO$_2$. Given a bias of -0.2 V vs. RHE, hydrogen evolution would likely be occurring, which will be depleting H$^+$ and forming more OH$^-$. This increase in pH could deprotonate the SiO$_x$H$_y$ ionic species and allow it to eventually form SiO$_2$.

Gaurav’s Comment: Basically, reduction of water at low pH leads to formation of OH$^-$ locally on the working electrode. This catalyzes SiO$_2$ condensation reaction which precipitates SiO$_2$ at the working electrode.