THIRD QUARTERLY REPORT

STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION OF THE ALKALINE SILVER ELECTRODE

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ABSTRACT

1. Equipotential maps for several electrode configurations have been drawn and related to current distribution and electrode geometry. Potential differences and solution resistivities have been plotted as functions of temperature. From these plots there appears to be an approximately linear relationship between potential difference and resistivity.

2. An extension of surface area determinations which includes sintered silver electrodes has been made. Data are presented which show the dependance of depth of penetration upon temperature.

3. Determinations of products of pyrolysis of sintered silver electrodes in high purity helium have altered slightly the conclusions of the previous report. The absence of low molecular weight hydrocarbons in these pyrolyses indicates that the residue is essentially carbonaceous in nature.
I. Potential Variations Over the Electrode Surface.

**Apparatus and Reagents**

Round electrodes 1.80 cm in diameter were used for most of the experiments. They were constructed of 99.99% pure silver foil 0.011 cm thick or of Yardney sintered silver plates 0.038 cm thick. Tygon lacquer was used to coat parts of the electrodes as shown in Figures 3a, 4a, and 6a. The counter electrode was platinum foil 2 x 2 cm. The electrolyte used in all experiments was 14.8 N NH₄OH to which 0.1 mole per liter KNO₃ was added.

The test cell and Luggin capillary measuring circuit were the same as described in the First Quarterly Report(3) page 1 and Figure 1, except that the L & N recorder was replaced by a Leeds & Northrup K-3 potentiometer. The constant current was supplied by a Hewlett-Packard model 881AX power supply. The current was adjusted to give the same current density, 3.53 ma/cm², in all experiments.

A standard conductivity cell and bridge measuring circuit were used for measuring conductivities.

**Potential Mapping Experiments**

Using the same technique described in the Second Quarterly Report(4) we constructed equipotential maps for six different electrode configurations undergoing oxidation in the ammoniacal electrolyte. The electrodes used are described below:

1. A round foil electrode 1.8 cm in diameter (Figure 1a)
2. A round electrode 1.8 cm in diameter cut from a Yardney sintered silver electrode (Figure 2a)
3. A round foil electrode identical to electrode No. 1 except that the reverse side was painted with Tygon lacquer to prevent any
reaction on that side (Figure 3a)

4. A round electrode whose back formed part of the cell wall was constructed by painting with Tygon all but a 1.8 cm circle located in the center of a 4.5 x 4.5 cm silver foil sealed in the end of the Haring cell. The counter electrode in this case was the 4.5 x 4.5 cm platinum foil sealed in the opposite end (Figure 4a)

5. A circular hole 0.64 cm in diameter was cut out of the center of a round 1.8 cm diameter foil electrode (Figure 5a)

6. A circle 0.64 cm in diameter was painted with Tygon on the center of both sides of a 1.8 cm diameter round foil electrode (Figure 6a)

The equipotential maps for electrodes 1 through 6 are Figures 1 through 6.

Comparison of Figures 1 and 2 for the solid and sintered electrodes indicates the same general potential variation. Near the edge of the sintered electrode the equipotentials are separated somewhat more than those near the edge of the solid electrode indicating a more moderate potential variation. This is probably because of the much greater surface area of the sintered electrode which would lead to less extreme variations in current density over its surface.

For the case where only one side of the electrode is available for reaction (electrode 3 Figure 3a) we also see a change in the equipotential lines near the edge as compared to the equipotential lines in Figure 1. The greater number of current paths directed toward the edge of a suspended electrode when the reverse side is non-reactive would account for this difference. In Figure 4 where these current paths around the reverse side are not available the equipotential patterns are much like those around the counter electrode side of the electrode in Figure 1.

Figures 5 and 6 show essentially the same equipotential patterns. Again consideration of the current paths available for each reaction site would enable one to explain the configuration of the equipotential maps.
Micrometer measurements taken of the thickness of electrodes after extensive oxidation in the ammoniacal electrolyte show that a significantly greater amount of reaction has taken place at the edge compared to the center. For example, center and edge measurements on a typical electrode were 0.17 mm and 0.11 mm, respectively.

$\Delta E$ As A Function of Conductivity

The $\Delta E$ was measured as a function of temperature with one capillary fixed at the center of a round Ag foil electrode and the other fixed 0.25 cm beyond the edge. The temperature of the ammoniacal electrolyte was adjusted to various values between 0° and 30°C.

The conductivity of the ammoniacal electrolyte was also measured as a function of temperature.

Plots of electrolyte resistivity ($\rho$) and of potential difference ($\Delta E$) versus temperature are shown in Figure 7. Figure 8 shows the linear relationship of $\Delta E$ and $\rho$.

For the range of resistivities plotted in Figure 8 the $\Delta E$ appears to change as does the resistivity of the solution.

Future Work

We propose the following:

1. A theoretical study of the relationship between current distribution and potential variation.


3. A comparison of the $\Delta E$'s in KOH with those in the ammoniacal electrolyte.
II. Surface Area Estimation

Depth of Penetration

As current is applied to a silver electrode in an alkaline solution the potential will rise to that of the Ag - Ag₂O reaction. The oxide first forms on the surface of the electrode and then penetrates the electrode as the reaction continues. The reaction will continue until the resistance of the oxide layer is high enough to cause the potential of the electrode to rise to that of the Ag₂O - AgO reaction. Measurement of the time required for this potential rise to occur permits calculation of the depth of penetration of the oxide layer by the following formula: \((2, 5)\)

\[
X = (K) \frac{I}{a} (t) = KD \ t
\]

Where:
- \(X\) = depth of penetration
- \(I/a\) = \(D\) = current density
- \(t\) = time required for potential rise
- \(K\) = conversion constant

If the assumption is made that at equal current densities the average depth of penetration will be equal for all surfaces, it then follows:

\[
X_1 = X_2 \text{ if } D_1 = D_2
\]

\[
X_1 = KD_1 \ t_1 = KD_2 \ t_2 = X_2
\]

Therefore

\[
t_1 = t_2
\]

This means that if two electrodes are oxidized under the same conditions, and the time required for the potential rise is the same, they were oxidized at the same current density.

A standard curve of known current density versus the time required for the potential rise to occur was plotted \((4)\) (see Figure 9). By varying the applied current until the time required for the potential rise matches a point on the standard curve one can find the current density and thus...
the surface area of the electrode.

**Surface Area Determinations**

Several types of surface areas have been estimated using this method. (See Table I) A curve similar to that of Figure 9 has been obtained for sintered silver electrodes. This is shown in Figure 10.

Much higher currents were used because of the increased surface area of these sintered electrodes. The roughness factors (the electrolytic surface area divided by the geometric area) of 62.8 and 71.2 reported in Table I were determined in the region of smaller current flow. At high values of the applied current the roughness factors became smaller. The values are shown in parentheses in Figure 10 for the particular time for potential rise, $t$, at which the comparison with Figure 9 was made. The variation of these roughness factors as a function of applied current (summarized also in Table II) is not unreasonable, for as the reaction is forced to go faster any internal shielding or electrolyte depletion would become more evident and thus affect the extent of the total reaction. This would tend to cut down the effective electrolytic surface. In order to lower the current ranges to that of our standard, two methods may be used. The first is to decrease the gross area of the sintered electrode. This will cause greater error in measurement of the geometric surface area, and also cause greater shielding from our electrical contact. The second method is to lower the temperature.

The data gathered on the temperature dependence of the depth of penetration indicate that lowering the temperature decreases the depth of penetration. Thus the decreasing of the depth of penetration is achieved by either lowering the temperature or increasing the applied current (see Figure 11). If the temperature is lowered, smaller currents within the range of the standard curve (Figure 9) may be used.
Future Work

1. Expand temperature range using standard and sintered electrodes.
2. Find range of currents which yield constant roughness factors for sintered electrodes.
3. Study other methods for comparing surface areas.
4. Study effect of cell geometry on surface area estimation.
III. Organic Residues in Sintered Silver Electrodes

In the previous report, (4) the model tentatively adopted was a sintered silver electrode containing a small amount of an organic residue part of which is characteristic of saturated hydrocarbons and part of which is more carbonaceous in nature which remains on the silver during pyrolysis in helium but which forms carbon dioxide when pyrolyzed in oxygen.

To answer questions concerning the effects of possible impurities in the helium carrier gas, we obtained a cylinder of helium from Matheson Company which was labeled "ultra high purity." Results of the pyrolysis of sintered silver in this high purity helium are shown as determinations 1 and 2 in Table III. Ethane and ethylene are not observed. The presence of ethane and ethylene in the pyrolyses reported previously (determination 3 in Table III) is probably due to reaction of the carbonaceous residue with the hydrogen present in the helium previously used as the carrier gas.

To account for the carbon monoxide and carbon dioxide observed (38 and 24 micrograms respectively per 1.0 gram of silver sample), we have assumed that oxygen is absorbed on the sample of sintered silver before pyrolysis. The amount of carbonaceous residue removed by pyrolysis in high purity helium is still less than one-tenth of that originally present as indicated in determination 4 of Table III.

Results of pyrolyses in hydrogen are shown as determinations 5, 6, and 7 of Table III. Methane is not resolved as a single component on the silica gel column. Therefore determination 7 with the molecular sieve column shows the amount of methane produced at the same temperature as that in determination 6.

Additional pyrolyses at 650°C in hydrogen were performed on samples of polyethylene, graphite, and polyethylene melted onto sintered silver. These results are shown in Table IV. The samples of polyethylene and graphite gave less methane than the sample of sintered silver.
However the polyethylene fused to sintered silver gave more methane than the polyethylene alone. The silver appears to catalyze the conversion to methane. Although these results suggest that either a polymethylene residue or a carbonaceous residue will give methane when pyrolyzed in hydrogen, the methane alone accounts for only a small part of the residue. The same conclusion probably applies to the ethane and ethylene produced.

The absence of low molecular weight hydrocarbons in the pyrolyses in helium points to a residue on sintered silver electrodes that is only carbonaceous in nature.

**Future Work**

Some additional experiments are planned in which samples of silver-polyethylene and silver-graphite will be pyrolyzed in oxygen, hydrogen, and helium. Comparison with data from sintered silver electrodes will give a better indication of the nature of the residue.
Table I

Surface Area Estimation

<table>
<thead>
<tr>
<th>Type of Surface</th>
<th>Current (µ amp)</th>
<th>Surface Area Geometric cm²</th>
<th>Surface Area Experimental cm²</th>
<th>Roughness Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver deposited upon glass disc (22 mm, dia.)</td>
<td>603</td>
<td>3.80</td>
<td>3.76</td>
<td>1.00</td>
</tr>
<tr>
<td>at three current densities</td>
<td>902</td>
<td>3.80</td>
<td>3.82</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>3.80</td>
<td>3.46</td>
<td>1.00</td>
</tr>
<tr>
<td>Unpolished silver foil, cleaned with soap and water, varied area and current density</td>
<td>602</td>
<td>2.54</td>
<td>3.30</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>602</td>
<td>2.54</td>
<td>2.79</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>6300</td>
<td>19.6</td>
<td>21.67</td>
<td>1.10</td>
</tr>
<tr>
<td>Silver wire, cleaned with soap and water. Current density constant</td>
<td>910</td>
<td>5.00</td>
<td>5.14</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>910</td>
<td>5.00</td>
<td>5.23</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>910</td>
<td>5.00</td>
<td>5.02</td>
<td>1.01</td>
</tr>
<tr>
<td>Sintered silver soaked in electrolyte for 10 min. Same current density</td>
<td>4900</td>
<td>.688</td>
<td>49.0</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>4900</td>
<td>.688</td>
<td>48.9</td>
<td>71.2</td>
</tr>
<tr>
<td></td>
<td>4900</td>
<td>.688</td>
<td>43.2</td>
<td>71.1</td>
</tr>
</tbody>
</table>
Table II
Sintered Silver Roughness Factors

<table>
<thead>
<tr>
<th>Applied Current (μ amp)</th>
<th>Geometric Area (cm²)</th>
<th>Roughness Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>12,000</td>
<td>.688</td>
<td>31.7</td>
</tr>
<tr>
<td>10,000</td>
<td>.688</td>
<td>34.2</td>
</tr>
<tr>
<td>8,000</td>
<td>.688</td>
<td>37.8</td>
</tr>
<tr>
<td>7,000</td>
<td>.688</td>
<td>46.6</td>
</tr>
<tr>
<td>6,000</td>
<td>.688</td>
<td>57.0</td>
</tr>
<tr>
<td>5,000</td>
<td>.688</td>
<td>68.2</td>
</tr>
<tr>
<td>4,500</td>
<td>.688</td>
<td>71.2</td>
</tr>
<tr>
<td>4,000</td>
<td>.688</td>
<td>67.8</td>
</tr>
</tbody>
</table>
Table III

Products from Pyrolyses of 1.0 gram Samples of Sintered Silver Electrodes (Delco Remy)

<table>
<thead>
<tr>
<th>Dtm.</th>
<th>Carrier Gas</th>
<th>Temp. °C</th>
<th>G. C. Column</th>
<th>Products (micrograms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Helium</td>
<td>540°</td>
<td>silica gel</td>
<td>CO  CH₄  C₂H₆  C₂H₄  CO₂</td>
</tr>
<tr>
<td></td>
<td>-high purity</td>
<td></td>
<td></td>
<td>0  0   24</td>
</tr>
<tr>
<td>2</td>
<td>Helium</td>
<td>500°</td>
<td>mol. sieve</td>
<td>30   0</td>
</tr>
<tr>
<td></td>
<td>-high purity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Helium</td>
<td>750°</td>
<td>silica gel</td>
<td>2.2  0.9  130</td>
</tr>
<tr>
<td></td>
<td>-commercial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Oxygen</td>
<td>500°</td>
<td>silica gel</td>
<td>0  0   520</td>
</tr>
<tr>
<td>5</td>
<td>Hydrogen</td>
<td>600°</td>
<td>silica gel</td>
<td>28   1   2   9</td>
</tr>
<tr>
<td>6</td>
<td>Hydrogen</td>
<td>650°</td>
<td>silica gel</td>
<td>29   12  3   13</td>
</tr>
<tr>
<td>7</td>
<td>Hydrogen</td>
<td>650°</td>
<td>mol. sieve</td>
<td>1.9</td>
</tr>
</tbody>
</table>
### Table IV

Methane as a Product From Pyrolysis of Various Solids in Hydrogen at 650°C

<table>
<thead>
<tr>
<th>Solid Sample</th>
<th>Weight</th>
<th>Methane* (micrograms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered silver</td>
<td>1.0 gram</td>
<td>1.9</td>
</tr>
<tr>
<td>Sintered silver with polyethylene</td>
<td>Ag - 1.0 gram (CH(<em>2)</em>\text{n}) 0.0015 gram</td>
<td>6.1</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.0015 gram</td>
<td>0.7</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.005 gram</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Molecular sieve column used in analysis*
Figure 1  Equipotentials around a working suspended silver foil electrode

Figure 1a  Diagram showing configuration of electrode used in Figure 1

Figure 2  Equipotentials around a working suspended sintered silver electrode

Figure 2a  Diagram showing configuration of electrode used in Figure 2
Figure 3. Equipotentials around a working suspended one-sided silver foil electrode.

5 mm on plot = 1 mm in cell

Figure 3a. Diagram showing configuration of electrode used in Figure 3.
Figure 4  Equipotential map of electrode having configuration shown below

5 mm on plot - 1 mm in cell

Figure 4a  Configuration of Tygon coated silver foil electrode
Figure 5  Equipotentials around a working suspended silver foil electrode with the center cut out.

Figure 5a Diagram showing configuration of electrode used in Figure 2.

Figure 6  Equipotential map of a working suspended silver electrode with the center painted with Tygon.

Figure 6a Diagram showing configuration of electrode used in Figure 2.
Figure 8  A plot of potential difference versus resistivity of solution. (Data from Figure 7.)
Figure 9 Time - current density relationship for electrodes of silver deposited upon glass discs. The time is the length of the first oxidation plateau.
Figure 10 Time-current relationship for sintered silver electrodes. Roughness factors are shown in parentheses.
Figure 11  Effect of temperature upon length of first oxidation plateau.  Current densities were identical in all cases.
References


