Analysis of Light and Dark Areas on Nickel-Hydrogen Plates

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ABSTRACT
Two distinct areas were observed on the positive plates of a nickel-hydrogen battery during teardown. The areas were gray and black in appearance. Plate material was removed from the two different areas and chemical analysis was performed. The results were compared with capacity measurements of the whole plates.

Introduction
Procedures for analysis of nickel plates in a battery are well established. In earlier times the analysis of nickel plates was only in the nickel-cadmium cell, but more recently it has been applied to nickel-hydrogen cells as well. The discharged form of the nickel plate is nickel hydroxide, Ni(OH)₂. This form can be related to discharged and charged material originally present on the plate. The chemical analysis procedure allows this distinction. Metallic nickel and cobalt are determined and their significance will be discussed later. The final calculations give results that are in terms of plate capacity.

Plate Appearance
During teardown of one particular nickel-hydrogen cell it was noted that the nickel plates had two distinct areas. One area was gray in color and started at the tab and radiated outward to the edge of the plate. The remaining area was black in appearance. The gray area accounted for one third of the total plate material and the remainder was black.

Sample Preparation
Two plates were dried, weighed and the light and dark areas were cut apart to make separate samples. The plate material was carefully removed and the grid was weighed. Total active plate material was obtained by subtracting total plate weight from total grid weight. The material removed was gently ground to facilitate dissolution during the chemical analysis procedure.

Chemical Analysis
The analytical procedure consisted of four determinations. All other results such as ampere-hours were calculated from these determinations. One procedure gave the weight of the charged positive plate material as nickel hydroxide, Ni(OH)₂. Another determination involved analysis of total plate active material as nickel hydroxide. The metallic nickel was determined in the positive plate and cobalt was obtained by inductively coupled plasma spectroscopy (ICP). The quantity of discharged material is found by subtracting the charged material from the total plate active material.

Charged Material
The charged material in a positive plate is in the form of NiOOH and NiO₂. The finely divided plate material is treated with a weighed amount of ferrous ammonium sulfate in an acetic acid solution. A reduction of higher valent nickel to divalent nickel occurs as the ferrous iron is oxidized to ferric iron according to the following reactions:

\[
\begin{align*}
\text{NiOOH} + \text{Fe}^{2+} + 3\text{H}^+ &= \text{Ni}^{2+} + \text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\text{NiO}_2 + 2\text{Fe}^{2+} + 4\text{H}^+ &= \text{Ni}^{2+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O}
\end{align*}
\]

The excess of ferrous iron in solution is then titrated with standard potassium permanganate solution:

\[
5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ = 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]
Total Plate Active Material and Metallic Nickel

The plate material was weighed then leached in acetic acid. Hydrazine sulfate is added to prevent the metallic nickel from dissolving. The soluble nickel is titrated with standard EDTA solution. This titration provides the total plate active material calculated as nickel hydroxide. During the dissolution step the metallic nickel adheres to the magnetic stirring bar and is removed. The stirring bar and adhering nickel are placed in contact with nitric acid. The dissolved nickel is titrated with standard EDTA solution for determination of the total metallic nickel. As mentioned before the total discharged material is found by subtracting the charged material from the total active material.

Cobalt Analysis

The powdered plate material was dissolved in nitric acid and diluted to 100mls for analysis by ICP.

Results

The chemical analysis data are tabulated below using designations from the nickel-cadmium procedure. Those designations are identified below the table.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( W_{cpp} )</th>
<th>( W_{cpp} )</th>
<th>( W_{app} )</th>
<th>( W_{cpp} )</th>
<th>( C_{cpp} )</th>
<th>( C_{cpp} )</th>
<th>( C_{cpp} )</th>
<th>% Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 lt area</td>
<td>4.469</td>
<td>1.832</td>
<td>2.637</td>
<td>4.423</td>
<td>0.529</td>
<td>0.762</td>
<td>1.29</td>
<td>2.12</td>
</tr>
<tr>
<td>23 dk area</td>
<td>4.266</td>
<td>1.404</td>
<td>2.862</td>
<td>4.654</td>
<td>0.406</td>
<td>0.827</td>
<td>1.23</td>
<td>2.08</td>
</tr>
<tr>
<td>39 lt area</td>
<td>4.599</td>
<td>2.030</td>
<td>2.569</td>
<td>4.432</td>
<td>0.587</td>
<td>0.742</td>
<td>1.33</td>
<td>2.27</td>
</tr>
<tr>
<td>39 dk area</td>
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<td>2.842</td>
<td>4.718</td>
<td>0.413</td>
<td>0.821</td>
<td>1.23</td>
<td>2.04</td>
</tr>
</tbody>
</table>

\( W_{cpp} \) = weight of total plate active material as nickel hydroxide
\( W_{cpp} \) = weight of charged positive plate material as nickel hydroxide
\( W_{app} \) = weight of discharged positive plate material as nickel hydroxide
\( W_{cpp} \) = weight of metallic nickel in positive plate
\( C_{cpp} \) = capacity of charged positive plate material
\( C_{cpp} \) = capacity of discharged positive plate material
\( C_{cpp} \) = total capacity of positive plate active material

Plate No. 23 had 1.253 ampere-hours
Plate No. 39 had 1.263 ampere-hours

Discussion

The difference in composition between the light and dark areas is obvious from the tabulated data. An unevenness of discharging is shown by the presence of more charged material on the plate that is in direct contact with the tab. The light area which extends out from the tab amounts to about one third of the total plate area. The dark area on both plates tested contained more discharged material and consequently less charged material than the light area. Likewise the metallic nickel was more in the dark area than the light area. Cobalt was determined in the light and dark areas in order to see if trends exist. Less nickel in the sinter should signal there is more corrosion in that area of the plate and thus there should be less cobalt as well. The cobalt turned out to be less in the dark area than in the light area by a small amount. This is the opposite of what should be expected if corrosion was taking place in the area of the plate with the most charged material. Plate capacity as calculated from the chemical data turned out to agree very well with actual capacity testing using other plates from the cell.
Conclusions

The analysis of the different areas of the plates shows how valuable chemical analysis of the active material can be. This work has shown there is an unevenness of charging and discharging going on. Since the distribution of cobalt between the light and dark areas did not show the same trend as nickel metal the cobalt alone cannot be used as a measure of corrosion. The action during cycling is far from homogeneous over the entire plate. Cobalt has been known to move around during cycling so an analysis of new plates would be needed. From this a further understanding can perhaps be gained of the chemical and physical actions going on during cycling. Any such information is needed for cell design considerations.

Acknowledgements

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References
