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Cycle Life Test and Failure Model of Nickel-Hydrogen Cells

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Cycle Life Test and Failure Model of Nickel-Hydrogen Cells

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Abstract

COMSAT, and Air Force/Hughes design six-ampere-hour individual pressure vessel nickel-hydrogen cells were charge/discharge cycled to failure. Failure was defined to occur when the end of discharge voltage degraded to 0.9 volts. They were cycled on a low-earth-orbit cycle regime to a deep depth of discharge (80 percent of rated ampere-hour capacity). Both cell designs were fabricated by the same manufacturer and represent current state-of-the-art cells. A failure model was advanced which suggests both cell designs have inadequate volume tolerance characteristics. The limited existing data base, at a deep depth of discharge (800) was expanded. Two cells of each design were cycled. One COMSAT cell failed at cycle 1712 and the other failed at cycle 1875. For the Air Force/Hughes cells, one cell failed at cycle 2250 and the other failed at cycle 2638. All cells, of both designs, failed due to low end of discharge voltage. No cell failed due to electrical shorts. After cell failure, three different reconditioning tests (deep discharge, physical reorientation, and open circuit voltage stand) were conducted on all cells. A fourth reconditioning test (electrolyte addition) was conducted on one cell of each design. In addition, post-cycle cell teardown and failure analysis were performed on the one cell of each design which did not have electrolyte added after failure. These tests were conducted to evaluate failure modes. Based on the reconditioning and post-cycle cell teardowns and analysis tests, the failure model advanced for the COMSAT cell design is that the nickel electrode increased in volume, resulting in inadequate electrolyte volume and thus, poor cell performance. The failure model advanced for the Air Force/Hughes cell design consists of two main factors: 1) the nickel electrode increased in volume, resulting in inadequate electrolyte volume which caused poor performance (recoverable by electrolyte addition), and 2) a degradation of the nickel electrode capacity which was not recoverable by electrolyte addition (flooded beaker test confirmed, 13 percent capacity degradation).

Introduction

Cycle life of nickel-hydrogen cells will effect their acceptance as a viable space energy storage system. Limited available cycle life data on nickel-hydrogen cells indicate that the state of development is such that it is probably adequate for geosynchronous earth orbit applications. However, for the more demanding low-earth-orbit applications, the current cycle life of about 2000 to 13000 cycles is not acceptable (1,2).

Some investigators report that this limited cycle life is mainly due to degradation of the nickel electrode. Some possible causes of degradation are: 1) density change of the active material during charge/discharge cycling may cause mechanical fatigue of the nickel plaque resulting in capacity loss (3), and 2) active material may flake or extrude from the electrode causing a loss of capacity and possibly shorting the cell (1,4). Extrusion of active material may also cause channeling of oxygen generated during charge. This channeling could lead to a "popping" phenomenon caused by large concentrations of oxygen reacting with hydrogen at the hydrogen electrode (4). The popping could damage the hydrogen electrode (3). Blistering of the nickel electrode during cycling could cause capacity loss (5).

In this report, results of cycle testing of six-ampere-hour COMSAT and Air Force/Hughes design individual pressure vessel nickel-hydrogen cells to failure are presented. A nickel hydrogen cell failure model is advanced for each cell design based on the cycle life and post-cycle failure analysis results.

Experimental

Test facility

The test facility used to cycle life test the nickel hydrogen cells is illustrated in Fig. 1. The facility design incorporates two main features: safety and versatility. Since the nickel-hydrogen cells are precharged with hydrogen and also generate hydrogen during charge, special attention was given to personnel safety. The cells were located on top of the instrumentation cabinets. There were two cells for each cabinet. Each cell was located within a cylindrical shrapnel shield in case of the improbable event of an explosion or rupture of the cell pressure vessel. During a test, the cylindrical shield was purged with nitrogen to create an inert atmosphere. The nitrogen gas, and hydrogen gas if any, would be exhausted from the test laboratory
Hughes cell is designed for LEO applications, but a maximum of twelve cells can be tested at the same time. The nickel charge and discharge time for selected cycles. A cell discharge current is controlled by an exhaust fan would fail or the nitrogen purge would reenter between the hydrogen electrodes to combine chemically. The facility's versatility allows for testing over a wide range of cycle regimes. A geosynchronous earth orbit (GEO) cycle regime can be run in real time using a programmable timer. Various accelerated GEO and low earth orbit cycle regimes can be run using a Texas Instrument timer. The cell discharge current is controlled by an electronic load, which can be varied from 0 to 100 amps. The charge current can also be varied in the same range. Test data is printed out locally using a Fluke data collector. Strip chart recorders are used to record cell voltage, current, and pressure as a continuous function of charge and discharge time for selected cycles. A maximum of twelve cells can be tested at the same time.

Test cell description

Two differently designed six-amper-hour individual pressure vessel nickel-hydrogen boiler plate cells, representing current state-of-the-art, were cycle life tested. They were the COMSAT (no wall wick) and the Air Force/Hughes (recirculation stack) cell designs. The COMSAT cell is designed for GEO applications. The Air Force/Hughes cell is designed for LEO applications, but is considered to be an all orbit cell.

The COMSAT cell design is illustrated in Fig. 2. It consists of a stack of nickel electrodes, separators, hydrogen electrodes, and gas screens assembled in a back-to-back electrode configuration and packaged in a pressure vessel. The electrodes are connected electrically in parallel. There are six nickel electrodes and seven hydrogen electrodes. In this back-to-back configuration the same type of electrodes directly face each other. Hence, oxygen generated at the nickel electrodes on charge leaves the stack between the back-to-back nickel electrodes and reenters between the hydrogen electrodes to combine chemically with hydrogen at the catalyzed hydrogen electrodes. This cell did not utilize a wall wick for electrolyte management. The nickel electrode plaques were fabricated by the slurry process and were electrochemically impregnated with active material by the Bell process. The separators were asbestos and the gas screens were polypropylene. The cells, prior to cycling, were precharged with hydrogen gas to a pressure of 50 PSIG.

The Air Force/Hughes design (recirculating stack) cell is illustrated in Fig. 3. It consists of a stack of nickel electrodes, separators, hydrogen electrodes, and gas screens assembled in a non back-to-back electrode configuration, which is packaged in a pressure vessel. The electrodes are connected electrically in parallel. In this configuration the electrodes of different types directly face each other. Hence, the oxygen generated at the nickel electrodes on charge has a direct path to the hydrogen electrodes, where it recombines chemically. This arrangement facilitates oxygen recombination. The inner surface of the pressure vessel is coated with zirconium oxide, which serves as a wall wick. The asbestos separators are extended beyond the electrodes to contact the wall wick. Hence, electrolyte which leaves the stack during cycling will be wicked back into the stack. The nickel electrode plaques were fabricated by the dry powder process and were electrochemically impregnated by the Pickett process. The separators were asbestos and the gas screens were polypropylene. The cells, prior to cycling, were precharged with hydrogen gas to a pressure of 50 PSIG.

Measurements and Procedure

For this experiment the quantities measured for each cell at the end of charge and discharge, and their accuracies were: Current (+ 0.3 percent), voltage (+ 0.5 percent), pressure (+ 1 percent), and temperature (+ 1 C limit of error). Additional measurements were charge and discharge ampere-hours (+ 0.5 percent), and charge to discharge ampere-hour ratio. Cell current, voltage, pressure and temperature were recorded continuously as a function of time, for selected cycles, on a strip chart recorder.

Cell charge and discharge currents were measured across a shunt, using an integrating digital voltmeter. Cell voltage was also measured using an integrating digital voltmeter. Cell pressure was measured using a conventional pressure transducer. Temperature was measured using an iron-constantan thermocouple located on the center of the outside pressure vessel wall. The thermocouple was mounted using a heat sink compound to insure good thermal contact. Charge and discharge ampere-hours were measured using a conventional ampere-hour meter. Charge to discharge ratio (ampere-hours into cell on charge to ampere-hours out on discharge) was calculated from the ampere-hour measurements.

Both cell types were charge/discharge cycled to failure, on a LEO cycle regime, to a deep-deep-of-discharge (80 percent of rated ampere-hour capacity). For this test cell failure was defined to occur, when the discharge voltage degraded to 0.9 volts during the course of a constant current 35-minute discharge at the 1.37C rate. In actual nickel hydrogen cell space energy storage applications, a minimum of 1 volt per cell was chosen as the cutoff, or failure voltage, because below 1 volt the cell discharge voltage drops rapidly. The power conditioning system was designed to this value. Prior to cycle testing the cells underwent 6 conditioning cycles. For the first test cycle, the cells were charged for eighteen hours at a C/10 rate (0.6 amps) followed by discharge at the 1.37C rate for 35 minutes. Then the normal LEO charge/discharge regime was initiated which consisted of charging the cells at about a constant 0.92C rate (5.5 amps) for 55 minutes immediately followed by discharge at a constant 1.37C rate (8.2 amps) for 35 minutes.
The charge to discharge ratio was initially set at 1.05 and was gradually increased as the cycling progressed to a final value of 1.10 in an attempt to improve cell performance.

The cell temperature was not controlled during the cycle test. The beginning of life temperature, on the average, for the COMSAT design cells was about 26°C, and for the Air Force/Hughes design cells was about 28°C. The cell temperature, for both designs, increased during cycling to an end of life temperature of about 29°C.

Two cells of each design were cycled. The Comsat cells were numbered 5 and 6. The Air Force cells were numbered 2 and 3. In addition, one cell of each design that was not cycled served as a control cell. After cell failure three different reconditioning tests (deep discharge, physical reorientation, and open circuit voltage stand) were conducted on all cells of each design.

A fourth reconditioning test (electrolyte addition) was conducted on cells 3 and 6. Post-cycle cell teardown and analysis were performed on cells 2 and 5 to evaluate failure modes.

The reconditioning tests are described as follows: 1) Deep discharge - Cells were discharged at C/5 rate to 0.006 volts, then a 1 ohm resistor was placed across each cell for 24 hours, 2) Physical reorientation - Cells were placed on side, rolled and left on side for 72 hours, 3) Open circuit voltage stand - Cells were left on open circuit stand for 30 days. The purpose of this test was to allow water on the pressure vessel wall, if any, to return to the stack as a vapor and condense (isopiestic effect). 4) Electrolyte addition - 31 percent KOH was added to one cell of each design, and the excess electrolyte drained (about 28 ml remained in each cell).

Post-cycle cell teardown and failure analysis tests were performed on the cell of each design (cells 2 and 3) which did not have electrolyte added after failure. The failure analysis consisted of visual inspection of the following: 1) the inner surface of the pressure vessel for electrolyte, 2) the stack and stack components for electrolyte content and damage, 3) the separator for integrity, and 4) the hydrogen electrodes for flooding and damage due to the "popping" phenomenon. One cell of each design, which was not cycled, also underwent teardown and visual inspection. These cells served as reference points for comparison of the cycled cells. The thickness and electrolyte uptake of the cycled nickel electrodes, for each cell design, were compared to similar electrodes taken from the uncycled cells. The flooded capacity (beaker tests) of the cycled and uncycled electrodes were measured and compared. For the beaker test the counter electrode was an oversized nickel electrode, the reference electrode was Hg/HgO, and the electrolyte was a 31 percent KOH solution. The capacity was measured at the 1.37C discharge rate.

The results of post-cycle teardown and failure analysis of the COMSAT cell design, which did not have electrolyte added after failure, are summarized in Table 2. Visual inspection confirmed that there was no electrolyte on the inner surface of the pressure vessel and that the stack was dry. Precycle teardown, and visual inspection, of an as-received, similar control cell, revealed that the stack was not dry. Which raises the question: What happened to the electrolyte during cycling? The answer to this question could lie in the expansion of the nickel electrode. The nickel electrode (Bell process) increased in thickness on the average about 20 percent and also increased in the amount of electrolyte absorbed by about 20 percent compared to similar but uncycled electrodes. The increase in electrolyte absorption was probably caused by the increase in pore volume due to the electrode expansion. This probably occurred as follows. The nickel electrodes expanded and compressed the separators. The electrolyte forced out of the separators was absorbed by the electrodes. Additional electrolyte could have been extracted from the separators by capillary action, provided the proper relative pore size distributions existed between the stack components. Hence, expansion of the nickel electrodes effected electrolyte volume (as a percentage of stack saturation) and electrolyte distribution. Furthermore, stack resistance and cell performance are sensitive to stack electrolyte volume and distribution. For example, in nickel hydrogen
The cycle life of the COMSAT cell design should be significantly extended by incorporating extra electrolyte in the pressure vessel and a means of transporting it to the stack, thus maintaining the stack electrolyte volume at the proper level when the nickel electrode expands. A zirconium oxide wall wick and separators extended to contact it could serve as an electrolyte transport wick, as is the case in the Air Force cell design.

Air Force/Hughes cells. Results of the Air Force/Hughes cell design cycle life test are summarized in Table IV. One of the cells failed at cycle 2250. The other failed at cycle 2638. The failure of both cells was characterized by degradation of discharge voltage to 0.9 volts. Neither cell failed due to electrical shorts. The depth-of-discharge was 80 percent of the rated capacity. The measured and rated capacity was the same. Hence, the cells were cycled to 80 percent of measured capacity.

In Fig. 5 the effect of cycling and reconditioning on the end of discharge voltage for a representative Air Force/Hughes six-ampere-hour cell is shown. The cell failed at cycle 2250. After failure the same reconditioning tests, as performed on the COMSAT cell, were performed on this Air Force/Hughes cell. The first three reconditioning tests had little or no beneficial effect on cell performance which is similar to the results for the COMSAT cell. However, the addition of electrolyte resulted in only a partial recovery in end of discharge voltage. This cell was placed back on test and again failed after about 300 cycles (end of discharge voltage 0.9 volts). The reconditioning test results suggest that there was little or no electrolyte on the inner surface of the pressure vessel, that the stack was dry, and that there was other non-electrolyte related degradation since there was only a partial recovery in end of discharge voltage.

Results of post-cycle teardown and failure analysis of the Air Force/Hughes cell design which did not have electrolyte added after failure are summarized in Table V. Visual inspection confirmed that there was no electrolyte on the inner surface of the pressure vessel and that the stack was relatively dry (but not as dry as the COMSAT cell stack). Pre-cycle teardown and visual inspection of an as-received, similar control cell revealed that the stack was not dry. The nickel electrode (Pickett process) increased in thickness on the average of about 5 percent compared to similar but uncycled electrodes. The electrode expansion increased the pore volume available for electrolyte and thus affected the electrolyte volume and distribution in the stack. This, in turn, could have contributed to poor cell performance, as in the COMSAT cell design. However, since the cell did not provide the original capacity on the electrolyte addition, there appears to be a portion of the degradation which is not recoverable and due to some other phenomenon. This was confirmed by the post-cycle flooded (beaker test) nickel electrode capacity test. The flooded ampere-hour capacity decreased about 13 percent compared to similar uncycled electrodes.

The Air Force/Hughes cell design failure model and basis of the model are summarized in Table VI. Based on the reconditioning test results, and post-cycle cell teardown and analysis, the failure model advanced for this cell design, consists of two main factors: 1) the nickel electrode increased in volume, causing inadequate electrolyte volume, which caused poor cell performance (recoverable by electrolyte addition), and 2) a degradation of the nickel electrode capacity which was not recoverable by electrolyte addition (flooded beaker test confirmed 13 percent capacity degradation).

These test results emphasize the importance of an adequate electrolyte reservoir inside the pressure vessel to make up for the extra electrolyte volume required when the nickel electrode expands. They also emphasize that additional technology development of the stack and components is required for long life at deep depths of discharge.

CONCLUDING REMARKS

Two COMSAT and two Air Force/Hughes design six-ampere-hour nickel-hydrogen boiler plate cells, representing current state of the art, were tested to failure. The cells were cycled on a low-earth-orbit cycle regime at a deep depth-of-discharge (80 percent of rated capacity). Cell failure for both designs was characterized by degradation of discharge voltage to 0.9 volts. No cell failed due to electrical shorts. Based on experimental results, a failure model was advanced for both cell designs. Results confirm further technology development of nickel-hydrogen cells is required for long life LEO applications at a deep-depth-of-discharge.

REFERENCES


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<tr>
<th>CELL</th>
<th>CELL DESIGN</th>
<th>CYCLE REGIME</th>
<th>% DOD</th>
<th>CYCLE AT (1)</th>
<th>TYPE FAILURE</th>
<th>STATUS</th>
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<td>5</td>
<td>COMSAT</td>
<td>LEO</td>
<td>80</td>
<td>1875</td>
<td>Degradation of of $V_{EOD}$ to 0.9 volts, no electrical shorts</td>
<td>Failed, teardown analysis</td>
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<td>6</td>
<td>COMSAT</td>
<td>LEO</td>
<td>80</td>
<td>1712</td>
<td>Degradation of of $V_{EOD}$ to 0.9 volts, no electrical shorts</td>
<td>Failed, electrolyte added, test continuing</td>
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(1) Cell failure defined as cycle at which end of discharge voltage ($V_{EOD}$) degrades to 0.9 volts
<table>
<thead>
<tr>
<th>ITEM</th>
<th>OBSERVATION</th>
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<tbody>
<tr>
<td>Visual Inspection</td>
<td></td>
</tr>
<tr>
<td>* Pressure Vessel Inner Surface</td>
<td>Dry, no free electrolyte</td>
</tr>
<tr>
<td>* Cell Components</td>
<td></td>
</tr>
<tr>
<td>** Nickel Electrode</td>
<td>Relatively dry, no blisters</td>
</tr>
<tr>
<td>** Hydrogen Electrode</td>
<td>No flooding, no damage due to &quot;popping&quot; phenomenon</td>
</tr>
<tr>
<td>** Separator</td>
<td>Relatively dry, black powder</td>
</tr>
<tr>
<td>** Nickel Electrode (1)</td>
<td></td>
</tr>
<tr>
<td>* Thickness Change</td>
<td>20% increase</td>
</tr>
<tr>
<td>* Electrolyte Absorption</td>
<td>20% increase</td>
</tr>
<tr>
<td>* Capacity Change (Flooded, Beaker)</td>
<td>No change</td>
</tr>
</tbody>
</table>

\(1\) Compared to similar uncycled nickel electrodes
### TABLE 3  SUMMARY OF COMSAT CELL DESIGN FAILURE MODEL

- **COMSAT DESIGN**
  - **Failure Model** - Nickel Electrode (Bell Process) Increased in Volume, Resulting in Inadequate Electrolyte Volume and Thus Poor Cell Performance
  - **Basis of Model**
    - Cell Reconditioned Tests - Indicate Dry Stack
    - Post-Cycle Cell Teardown Analysis - Cell Stack Dry, No Electrolyte on Pressure Vessel Walls
    - Precycle Teardown Analyses (As Received Cell) - Cell Stack Not Dry
    - Nickel Electrode Thickness, On the Average, Increased About 20% Due to Cycling
    - Electrolyte Absorption of Cycled Electrode About 20% Greater Than Uncycled Electrode
    - Flooded Nickel Electrode Ampere-Hour Capacity (Beaker Tests) - No Degradation Compared to Uncycled Electrode
    - Addition of Electrolyte (28 ML) to Cell Resulted in Recovery of End of Discharge Voltage to Beginning of Life Value
    - Cell Has Been Cycled for Over 1400 Additional Cycles Since Electrolyte Addition and is Performing Satisfactorily
<table>
<thead>
<tr>
<th>CELL</th>
<th>CELL DESIGN</th>
<th>CYCLE REGIME</th>
<th>% DOD</th>
<th>CYCLE AT (1)</th>
<th>TYPE FAILURE</th>
<th>STATUS</th>
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<td>2</td>
<td>Air Force</td>
<td>LEO</td>
<td>80</td>
<td>2638</td>
<td>Degradation of of $V_{EOD}$ to 0.9 volts, no electrical shorts</td>
<td>Failed, Teardown Analysis</td>
</tr>
<tr>
<td>3</td>
<td>Air Force</td>
<td>LEO</td>
<td>80</td>
<td>2250</td>
<td>Degradation of of $V_{EOD}$ to 0.9 volts, no electrical shorts</td>
<td>Failed, Electrolyte Added, Test Restarted, Failed After 300 Additional Cycles</td>
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</tbody>
</table>

(1) Cell failure defined as cycle at which end of discharge voltage ($V_{EOD}$) degrades to 0.9 volts
TABLE 5 SUMMARY OF RESULTS OF POST-CYCLE AIR FORCE/HUGHES
CELL TEARDOWN AND FAILURE ANALYSIS

<table>
<thead>
<tr>
<th>ITEM</th>
<th>OBSERVATION</th>
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<tbody>
<tr>
<td>Visual Inspection</td>
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</tr>
<tr>
<td>- Pressure Vessel Inner Surface</td>
<td>Dry, no free electrolyte</td>
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<td>- Cell Components</td>
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<td>- Nickel Electrode</td>
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<td>No flooding, no damage due to &quot;popping&quot; phenomenon</td>
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<td>- Separator</td>
<td>Relatively dry, black powder</td>
</tr>
<tr>
<td>Nickel Electrode(1)</td>
<td></td>
</tr>
<tr>
<td>- Thickness Change</td>
<td>5% increase</td>
</tr>
<tr>
<td>- Electrolyte Absorption</td>
<td>Not measured</td>
</tr>
<tr>
<td>- Capacity Change</td>
<td></td>
</tr>
<tr>
<td>(Flooded, Beaker)</td>
<td>13% decrease</td>
</tr>
</tbody>
</table>

(1) Compared to similar uncycled nickel electrodes
TABLE 6 SUMMARY OF AIR FORCE/HUGHES
CELL DESIGN FAILURE MODEL

AIR FORCE DESIGN
- Failure Model - Consists of Two Main Factors: 1) Nickel Electrode (Picket Process) Increased in Volume, Resulting in Inadequate Electrolyte Volume, Which Caused Poor Cell Performance (Recoverable by Electrolyte Addition) and 2) A Degradation of the Nickel Electrode Capacity Which Was Not Recoverable by Electrolyte Addition (Flooded Beaker Tests Confirm, 13% Capacity Degradation)

BASES OF MODEL
- Cell Reconditioned Tests - Indicate Dry Stack
- Post-Cycle Cell Teardown Analysis - Cell Stack Relatively Dry, Compared to Uncycled Cell, But Not as Dry as COMSAT Cell; No Electrolyte on Pressure Vessel Walls
- Precycle Teardown Analysis (As Received Cell) - Cell Stack Not Dry
- Nickel Electrode Thickness, On the Average, Increased About 5%
- Flooded Nickel Electrode Ampere-Hour Capacity (Beaker Tests) - Capacity Decreased 13% Compared to Uncycled Electrode
- Addition of Electrolyte (28 ML) to Cell Resulted in Partial Recovery of End of Discharge Voltage
- Cell Placed Back On Test and After About 300 Cycles Failed (End of Discharge Voltage 0.9 Volts)
Figure 1. - Nickel-hydrogen cell test facility.

Figure 2. - Illustration of Comsat design individual pressure vessel nickel-hydrogen cell.
Figure 3. - Illustration of Air Force/Hughes design individual pressure vessel nickel-hydrogen cell.

Figure 4. - Effect of charge/discharge cycling and recon- ditioning on end of discharge voltage of a representative 6 A-h Comsat design Ni/H₂ boiler plate cell.
Figure 5. Effect of charge/discharge cycling and reconditioning on end of discharge voltage of a representative 6 A-h Air Force/Hughes design Ni/H₂ boiler plate cell.