CAPACITY MANAGEMENT AND WALKDOWN DURING LEO CYCLING OF NICKEL-HYDROGEN CELLS AND BATTERIES

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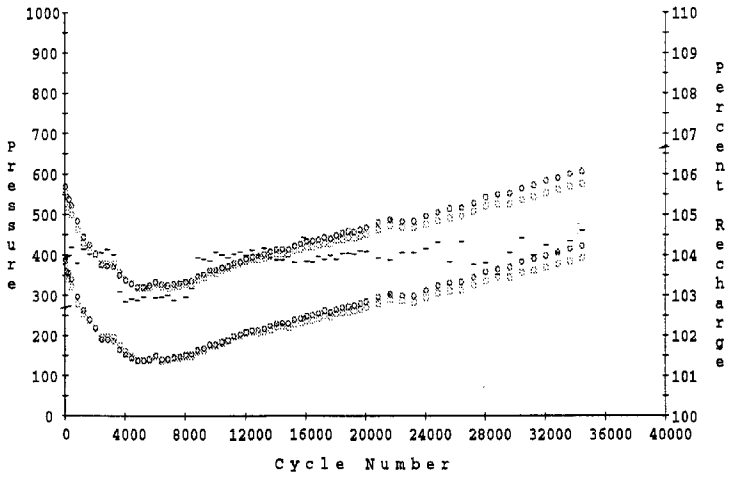
OUTLINE OF PRESENTATION

- CAPACITY WALKDOWN DEFINED AND ILLUSTRATED
- IMPORTANCE OF CAPACITY WALKDOWN
- FOUR APPROACHES TO UNDERSTANDING THE PHENOMENON
  - Pressure Trend Studies
  - Charging Curve Studies
  - Electrochemical Voltage Spectroscopy Studies
  - Destructive Physical Analysis Studies
- RESULTS OF THE INTERRELATED STUDIES
- SUGGESTED MECHANISM FOR CAPACITY WALKDOWN
- CHARGING PROTOCOLS TO AVOID THE PROBLEM
- SUMMARY STATEMENTS

CAPACITY WALKDOWN



Characteristics

- Very Slow
- 2000 - 8000 Cycles
- Recoverable
- 30% to 40%Capacity Loss
- Monitored Using Strain Gauge

IMPORTANCE OF CAPACITY WALKDOWN

- **RESULTS IN A SIGNIFICANT REDUCTION IN THE RESERVE CAPACITY FOLLOWING A NORMAL DISCHARGE**
  - **The Gradual Drop in State of Charge for a Fixed Depth of Discharge will Result in Less and Less Reserve Capacity Following a Discharge**
- **WHEN THE CHARGEING PROTOCOL IS BASED ON A FIXED RECHARGE RATIO ADJUSTMENTS ARE REQUIED AS CYCLING CONTINUES**
  - **Accuracy to the Nearest One Tenth of a Percent May be Needed**

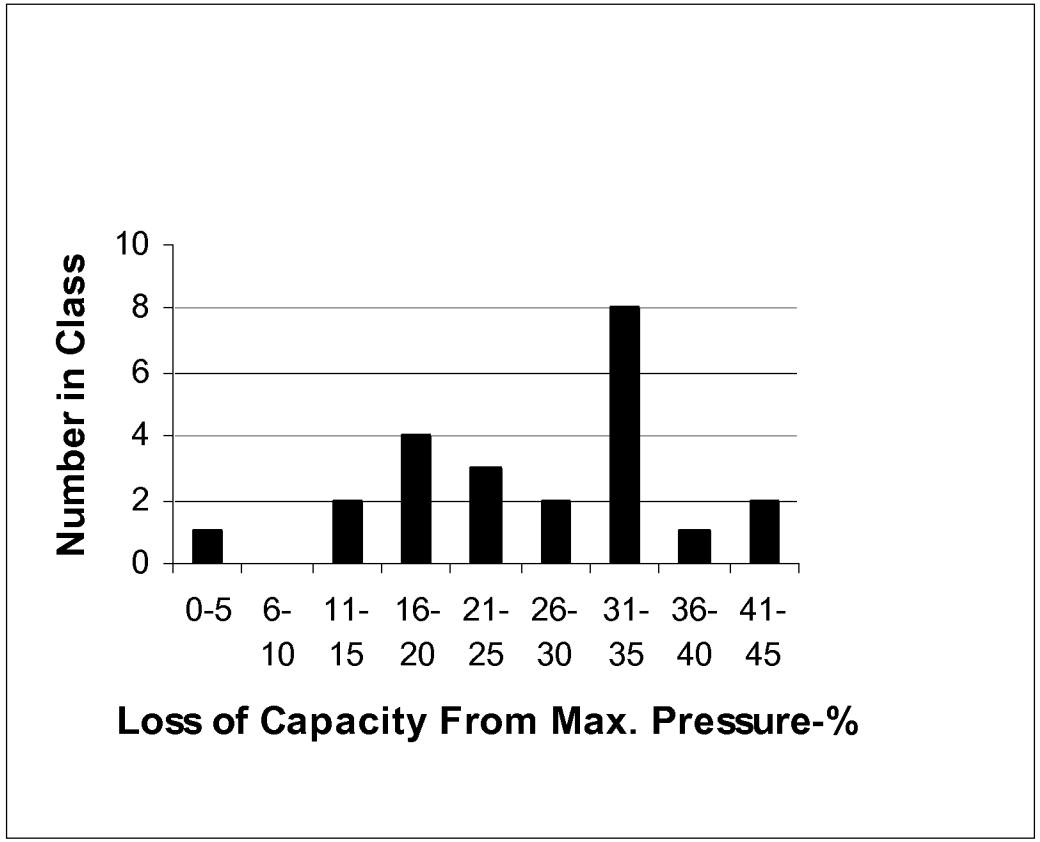
APPROACHES USED TO QUANTIFY AND UNDERSTAND CAPACITY WALKDOWN

- PRESSURE TRENDS DURING LEO CYCLING AT THE NAVY FACILITY AT CRANE INDANA
  - Air Force, NASA Glenn, and NASA Space Station Tests
- CHARGING CURVES OF SELECTED AIR FORCE AND NASA SPONSORED LEO TESTS
- ELECTROCHEMICAL VOLTAGE SPECTROSCOPY STUDIES OF SELECTED SAMPLES OF PLATE MATERIAL FROM A VARIETY OF SOURCES
- EXTENSIVE DESTRUCTIVE PHYSICAL ANALYSES ON SIMILAR CELLS
  - One Cycled Under Conditions With No Walkdown
  - One Cycled Under Conditions With Significant Amount of Walkdown

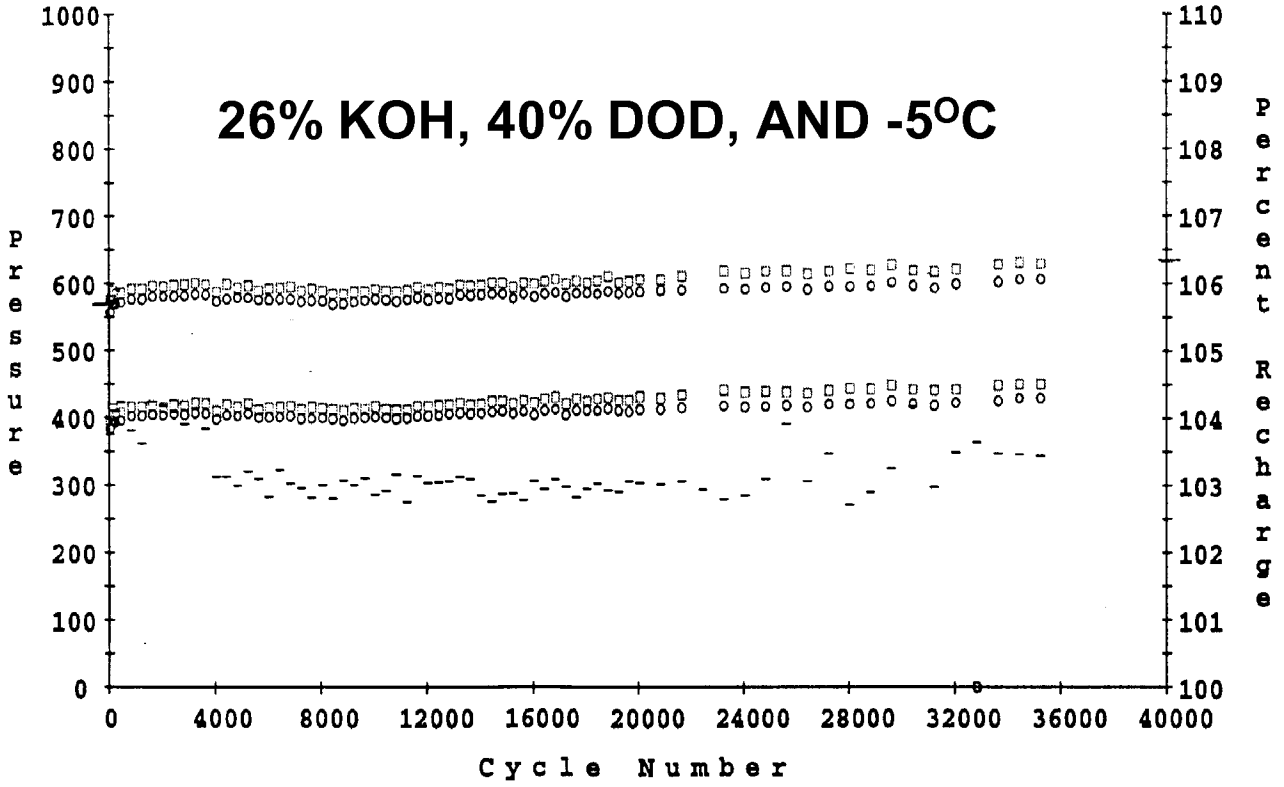
WALKDOWN AS A FUNCTION OF CYCLING CONDITIONS

- CELLS CYCLED AT 40% DOD AND -5^{O}C DID NOT SHOW WALKDOWN
- CELLS CYCLED AT 40% DOD AND +10^{O}C SHOWED VARIABLE AMOUNTS OF WALKDOWN
- CELLS CYCLED AT 60% DOD AND +10^{O}C SHOWED NO WALKDOWN
- CELLS CYCLED AT 60% DOD AND -5^{O}C SHOWED NO WALKDOWN BUT VERY SHORT CYCLE LIVES

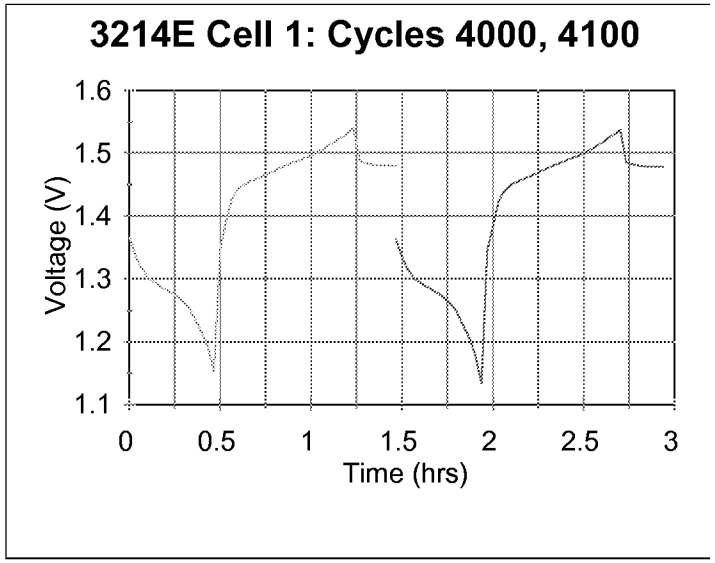
CAPACITY LOSS AT 40% DOD AND +10^{O}C

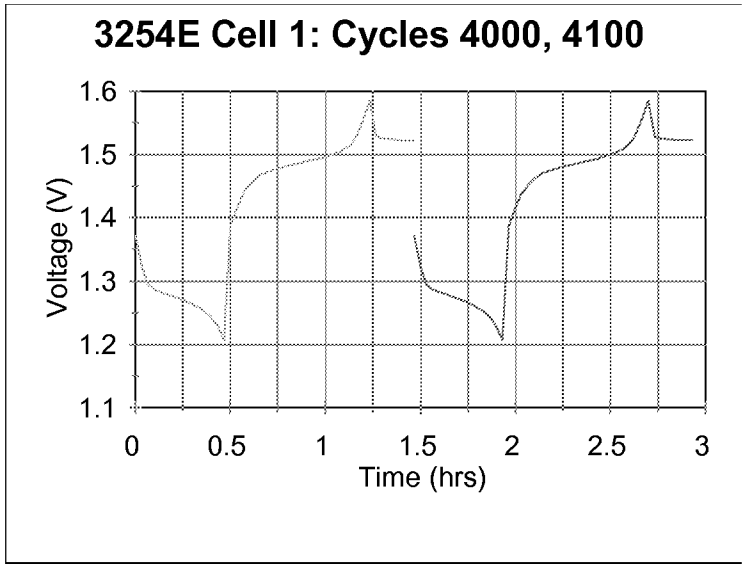


TYPICAL TEST SHOWING NO WALKDOWN



CHARGE CURVES FOR TWO CELLS: ONE AT +10°C AND ONE AT -5°C





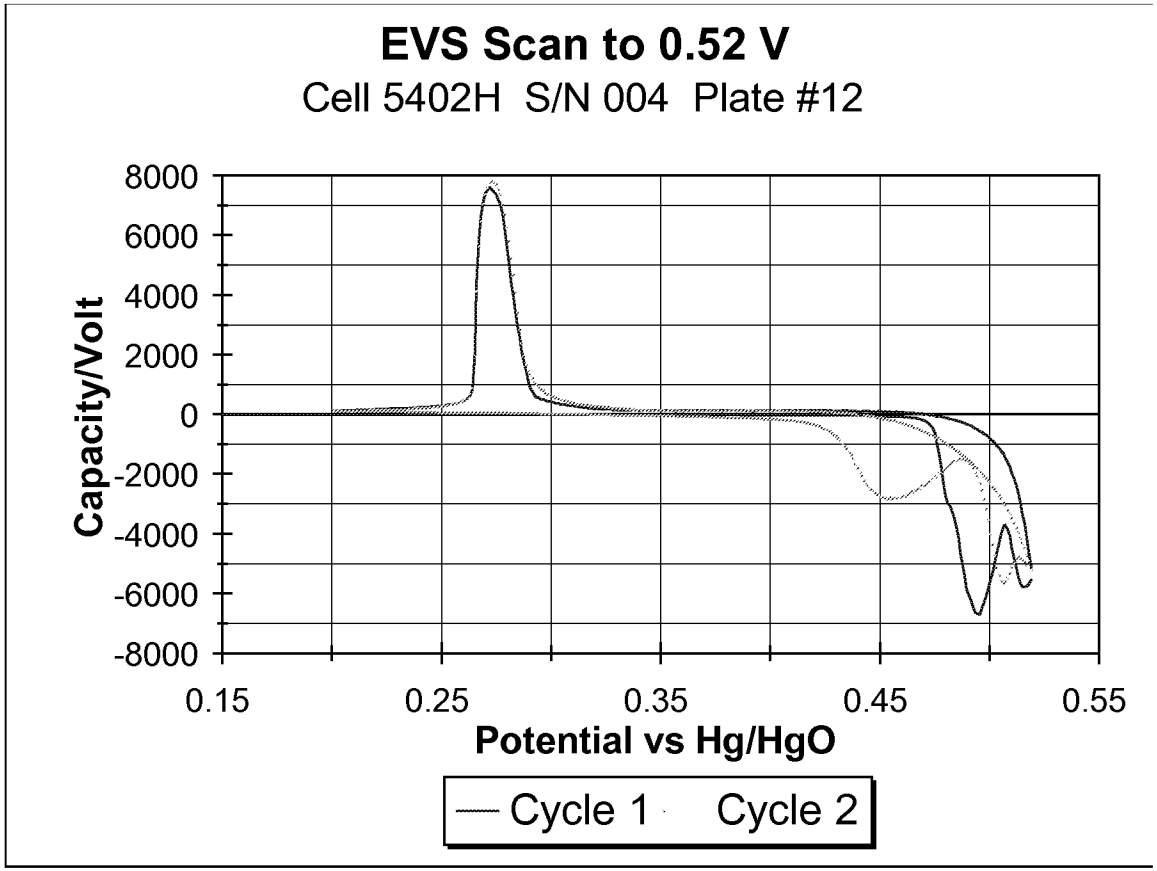
+10°C, 40% DOD, RR = 1.04

-5°C, 40% DOD, RR = 1.03

DIFFERENCES IN CHARGING CURVES

- CYCLE 4000 WAS NEAR THE MINIMUM OF PRESSURE FOLLOWING WALKDOWN FOR CELLS IN PACK 3214E
- CELL #1 IN PACK 3214E DOES NOT SHOW THE SHARP ROLLUP AT THE END OF THE CHARGING PROCESS
- CELL #1 IN PACK 3254E HAS A SHARP ROLLUP INDICATIVE OF LESS OXYGEN EVOLUTION
  - This Results in a Higher Charging Efficiency and Therefore a Higher State of Charge at the End of the Charging Process for the Cell Cycled at -5°C

ELECTROCHEMICAL VOLTAGE SPECTROSCOPY STUDIES



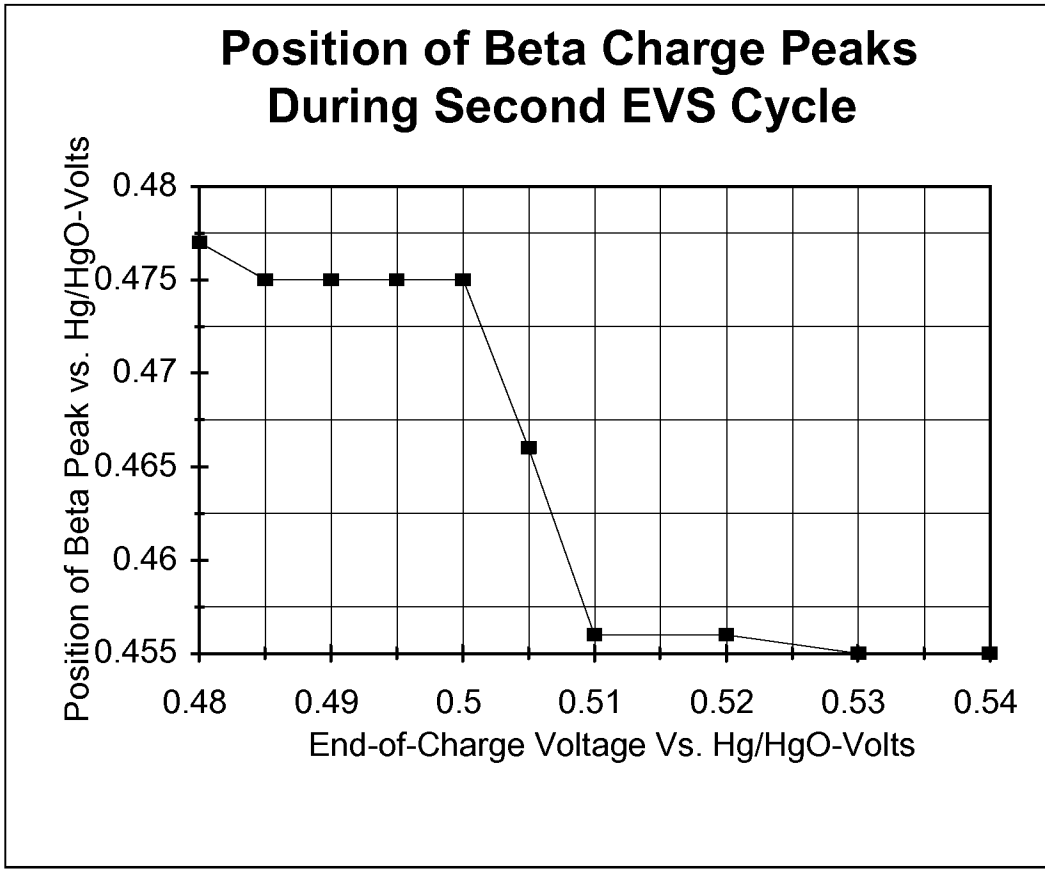
EVS REVEALED THE SOURCE OF THE WALKDOWN PHENOMENON

- THE BETA MATERIAL DURING THE FIRST CYCLE IS MORE DIFFICULT TO CHARGE BY 30 TO 40 MILLIVOLTS
- AFTER CHARGING TO THE GAMMA PHASE AND ONE FULL DISCHARGE, THE BETA MATERIAL IS REFERRED TO A BEING IN THE 'ACTIVE' FORM
- THE POSITION OF THE CHARGING PEAKS OF THE SECOND CYCLE IS INDICATIVE OF A DIFFERENT ACTIVE SPECIE
- IT HAS BEEN SUGGESTED THAT THEY ARE DIFFERENT CRYSTALINE FORMS OF BETA NICKEL HYDROXIDE
- WE HAVE NOT BEEN ABLE TO DESCERN ANY IDENTIFICABLE DIFFERENCES IN THE TWO DIFFERENT FORMS

RESULTS OF EVS SCANS TO DIFFERENT END OF CHARGE VOLTAGES

- MULTIPLE ~1.0 CM^2 SAMPLES SELECTED FROM THE SAME PLATE TAKEN FROM A GOOD CELL WITH ONLY 100 CYCLES
- TWO COMPLETE CHARGE DISCHARGE CYLES WERE USED AS PER THE PREVIOUS CHART
- THE END OF CHARGE VOLTAGE RANGED FROM 0.48 V vs. Hg/HgO REFERENCE ELECTRODE TO 0.54 V
- THE VOLTAGE PEAK FOR CHARGING THE BETA $Ni(OH)_2$ DURING THE SECOND CYCLE WAS RECORDED
- IT WAS FOUND THAT IF THE END OF CHARGE VOLTAGE WAS BELOW A CERTAIN VALUE, THE DISCHARGED FORM OF THE ACTIVE MATERIAL WAS NOT CONVERTED TO THE ACTIVE FORM
- FOR THIS ELECTRODE THE DIFFERENCE IN POTENTIAL OF THE TWO FORMS WAS 20 MILLIVOLTS

POSITION OF THE BETA PEAK DURING THE SECOND EVS SCAN



EXTENSIVE EVS STUDIES REVEALED THE FOLLOWING

- THE DEACTIVATED FORM OF NICKEL HYDROXIDE IS THE THERMDYNAMICALLY STABLE FORM
- THE ACTIVATED FORM OF NICKEL HYDROXIDE CAN BEGINE TO CONVERT BACK TO THE STABLE INACTIVE FORM IN ONLY A FEW DAYS
- ONCE IN THE ACTIVATED FORM, THE MATERIAL WILL REMAIN IN THE ACIVATED FORM AS LONG AS IT IS CHARGED ABOVE THE CRITICAL TRANSITION VOLTAGE
- THE DISCHARGE BETA AND GAMMA PEAKS SEPARATE AS ONE OR THE OTHER MATERIAL DOMINATES THE DISCHARGE TRACE

POST TEST AND DPA STUDIES ON SIMILAR CELLS

- CELL FROM PACK 3214E
  - +10 Degrees, 1.04 Recharge Ratio, 26% KOH
- CELL FROM PACK 3254E
  - -5 Degrees, 1.03 Recharge Ratio, 26% KOH
- CELLS WERE 50 Ah, DOUBLE LAYER ZIRCAR, SLURRY, BACK TO BACK CELLS CYCLING UNDER AIR FORCE SPONSORSHIP
- CELLS WITHDRAWN FROM ONGOING TESTS FOR OUR FURTHER STUDIES
- CRANE CONDUCTED TWO POST CEST CYCLES

SUMMARY OF CRANE POST TEST EVALUATION

Discharge	Charge	+10°C Cells	-5°C Cells
	Normal	1.04 recharge ratio	1.03 recharge ratio
C-rate		21.7 Ah discharged	46.8 Ah discharged
C/10-rate		11.3 Ah discharged	7.7 Ah discharged
Total 1st discharge		33.0 Ah discharged	54.5 Ah discharged
	C/2-rate	48.9 Ah charged	48.9 Ah charged
	C/10-rate	14.8 Ah charged	14.9 Ah charged
	Total 1st charge	63.7 Ah charged	63.8 Ah charged
C-rate		49.9 Ah discharged	50.2 Ah discharged
C/10-rate		7.7 Ah discharged	9.0 Ah discharged
Total 2ed Discharge		57.6 Ah discharged	59.2 Ah discharged

AEROSPACE DPA ACTIVITIES

- CELLS PUNCTURED IN SPECIAL CHAMBER TO MEASURE RESIDUAL GAS PRESSURE AND COMPARE WITH STRAIN GAUGE READINGS OF OTHER CELLS WITHIN THE PACK
- RESIDUAL GAS SAMPLES SENT FOR MASS SPEC. ANALYSIS
- FLOODED UTILIZATION AND EVS TESTING OF PLATE SAMPLES FROM FOUR SECTORS OF THE CELLS
- CHEMICAL ANALYSIS CARRIED OUT ON SINTER AND ACTIVE MATERIAL

RESIDUAL PRESSURE AND GAS ANALYSIS

Cell Pack	3214 E	3254 E
Cycling Temp. - ^{o}C	+ 10	-5
Residual Pressure - psia	118.0	1.3
Composition - %		
Hydrogen	97.8	3.0
Water Vapor	1.8	16.3
Nitrogen	0.3	77.9
Average Plate Expansion - %	15.7	15.0

SUGGESTED MECHANISM

- CHARGING TO HIGHER VOLTAGES CONVERTS BETA NICKEL OXYHYDROXIDE TO THE GAMMA PHASE
- UPON DISCHARGE, THE UNSTABLE ALPHA FORM OF NICKEL HYDROXIDE IS FORMED
- THIS MATERIAL DISSOLVES IN KOH AND PRECIPITATES AS A VERY SMALL CRYSTALINE FORM OF BETA NICKEL HYDROXIDE
- THIS IS THE ACTIVATED FORM AND CAN EASILY BE CHARGED TO THE GAMMA FORM VIA THE BETA NICKEL OXYHYDROXIDE
- OSTWOLD RIPENING CONVERTS THE ACTIVATED FORM BACK TO THE DEACTIVATED FORM
- LOWER TEMPERATURES FACILITATE THE CHARGING TO THE GAMMA PHASE AND RETARDS THE RATE OF COVERSION BACK TO THE DEACTIVATED FORM

SUGGEST RECHARGE PROTOCOL TO AVOID OR MINIMIZE WALKDOWN

- CYCLING TEMPERATURE MUST BE LOW ENOUGH TO PERMIT CHARGING TO THE GAMMA PHASE
- DETERMINE MINIMUM VOLTAGE REQUIRED TO CONVERT MATERIAL TO THE ACTIVE FORM
- CHARGE TO A CUTOFF PRESSURE OR MONITOR THE END OF CHARGE PRESSURE
- CORRECT PRESSURE READING FOR STRAIN GAUGE DRIFT AND SINTER CORROSION VIA RECONDITIONING

SUMMARY

- CAPACITY WALKDOWN A CONSEQUENCE OF THE INABILITY TO MAINTAIN A HIGHT STATE OF CHARGE
- CAPACITY LOSS IS TYPICALLY 35% WHICH WOULD BE EXPECTED BY THE VALENCE DIFFERNCE BETWEEN GAMMA AND BETA NICKEL OXYHYDROXIDE
- CYCLING AT -5 DEGREES FACILITATES THE FORMATION OF THE GAMMA PHASE
- EXCESSIVE OVERCHARGE CAN ALSO FACILITATE GAMMA PHASE FORMATION AT THE EXPENCE OF CYCLE LIFE
- CONDITIONS CAN NOW BE SUGGESTED TO HELP MINIMIZE CAPACITY WALKDOWN