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CHARACTERISTICS OF STORAGE RELATED CAPACITY LOSS IN NI/H_2 CELLS

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The changes in the capacity, voltage and pressure profile of flight configuration Ni/H_2 cells when they are stored for extended periods is examined in this manuscript. The Ni/H_2 cells exhibit capacity fade phenomenon regardless of their design when they are stored at room temperature. Capacity loss also occurs if old cells (5 years old) are stored in a very low rate trickle charge (C/200 rate) condition. Periodic recharge technique leads to pressure rise in the cells. Conventional trickle charge (C/100 rate) helps in minimizing or eliminating the second plateau which is one of the characteristics of the capacity fade phenomenon.

1992 NASA AEROSPACE BATTERY WORKSHOP

HUNTSVILLE, ALABAMA

CHARACTERISTICS OF STORAGE RELATED CAPACITY LOSS IN NI/H_2 CELLS

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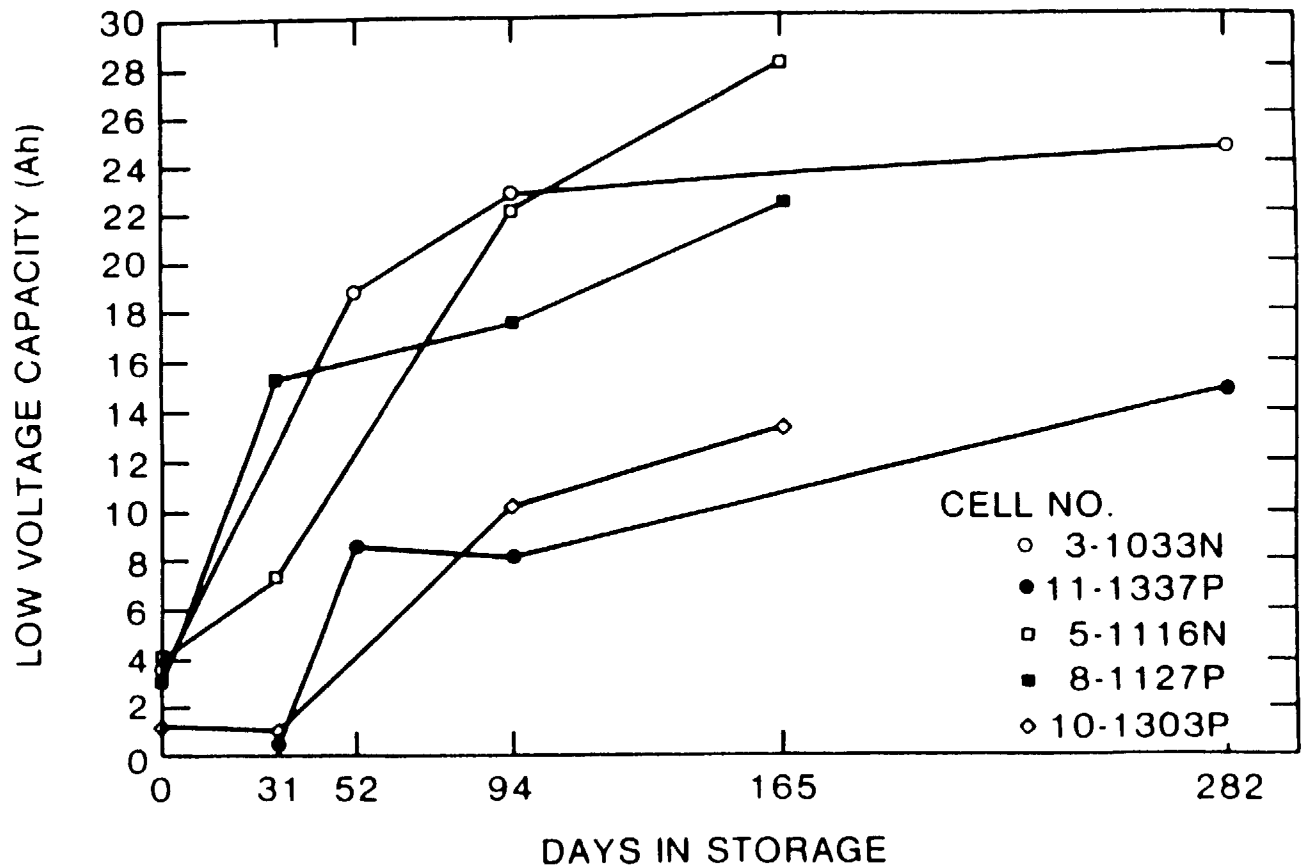
CAPACITY FADE AND RECOVERY IN VARIOUS CELL DESIGNS

CELL CAPACITY	DESIGN	ACTIVE MATERIAL LOADING g/cc	COEFFICIENT OF UTILIZATION OF POSITIVE IN FLOODED KOH (%)	COEFFICIENT OF UTILIZATION IN CELL (%)	KOH CONTENT gKOH/Ah	CAPACITY FADE AND RECOVERY
44 Ah	Alcohol/ Ni precharge	1.58	135	123	4.50	Fades extensively Recoverable with trickle charge In orbit battery recovered capacity
44 Ah	Alcohol/ Ni precharge	1.45	151	132	4.66	No fade in 3 months
30 Ah	Aqueous/ H2 Precharge	1.60	124	120	3.03	Flight battery Trickle charged to maintain capacity, showed excellent in orbit data
65 Ah	Aqueous/ H2 Precharge	1.57	112	102	2.74	Fades extensively
83 Ah	Aqueous/ H2 Precharge	1.66	118	107	2.85	Simple reconditioning recovers capacity
83 Ah	Aqueous/ Ni Precharge	1.56	130	123	4.40	No fade for 3 months

CAPACITY MAINTENANCE AT VARIOUS STORAGE CONDITIONS

STORAGE CONDITIONS	LENGTH OF STORAGE	CAPACITY BEHAVIOR
Open circuit Room temperature	12 months	Ni precharged cell showed one-third of the loss suffered by H2 precharge cells. Second plateau appears.
Open circuit 0°C	9 months	Capacity is maintained for 6 months.
Trickle charge at C/100 at 10°C	9 months	Not only maintains but also recovery capacity.
Recharge every 7 days	6 months	Maintains and recovery capacity. However there is a pressure rise.
Recharge every 14 days	6 months	Maintains capacity. Pressure rises.
Very low rate trickle charge C/290 at 0°C	6 months	Capacity declined for 5 year old batteries.

VARIATION OF ADDITIONAL CAPACITY AT LOW VOLTAGES WITH STORAGE TIME AT ROOM TEMPERATURE



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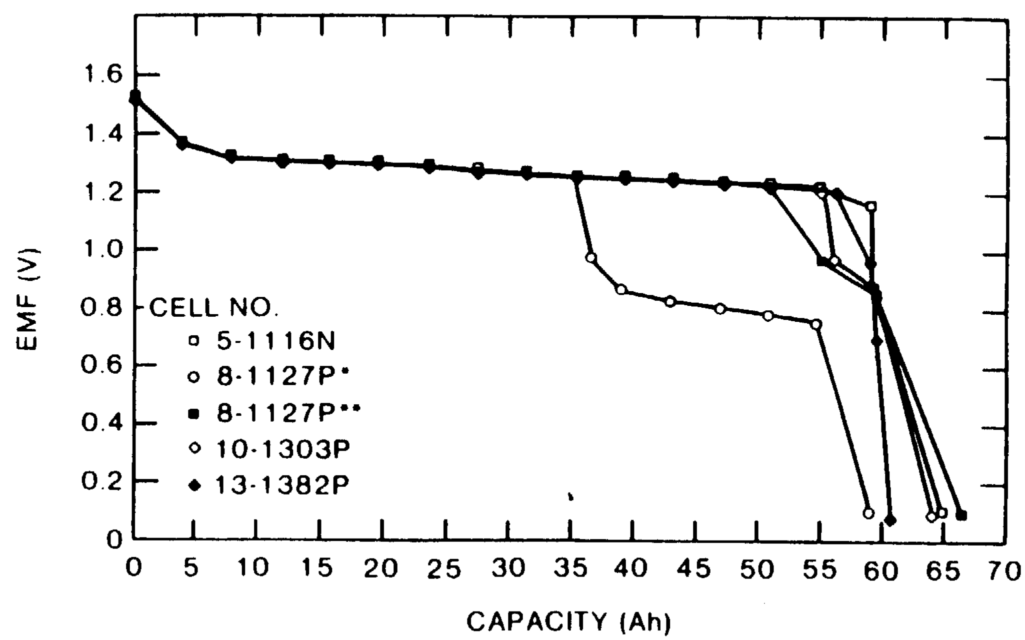
EMF PROFILE OF CELLS AT 23.5A DISCHARGE RATE AFTER TWO 6-WEEK PERIODS OF TOP-OFF CHARGE



* BEFORE TOP CHARGE
** AFTER TOP CHARGE

CAPACITY VARIATION AT -20°C

Cell No.	Precharge	Initial Capacity (to 1 V) (Ah)	Storage Period (days)	Final Capacity (to 1 V) (Ah)
4-1104N	H_2	63.6	270	66.0
5-1116N	H_2	60.7	270	67.2
13-1382P	None	66.7	112	66.3
1-1081N	H_2	59.9	112	60.3

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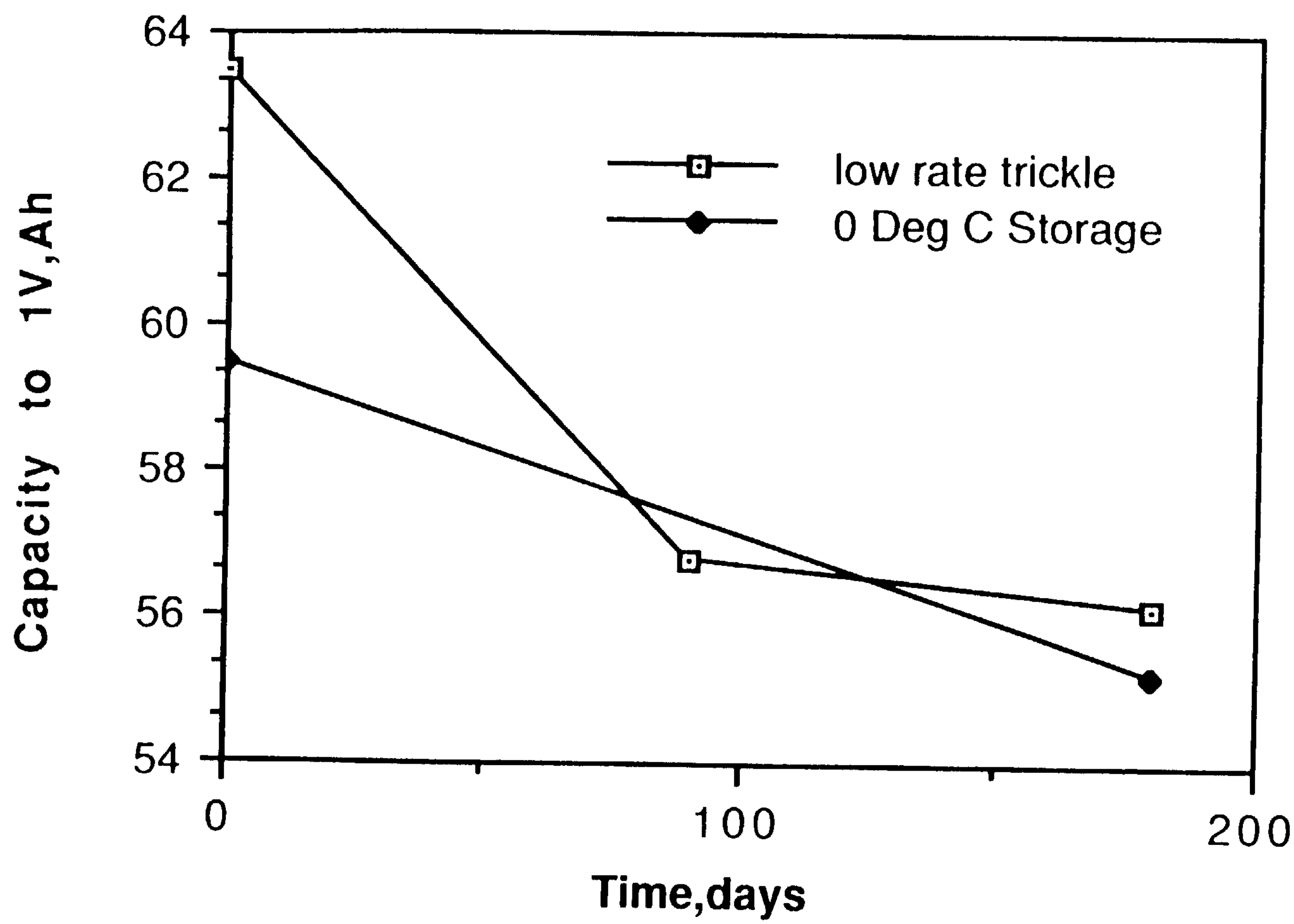
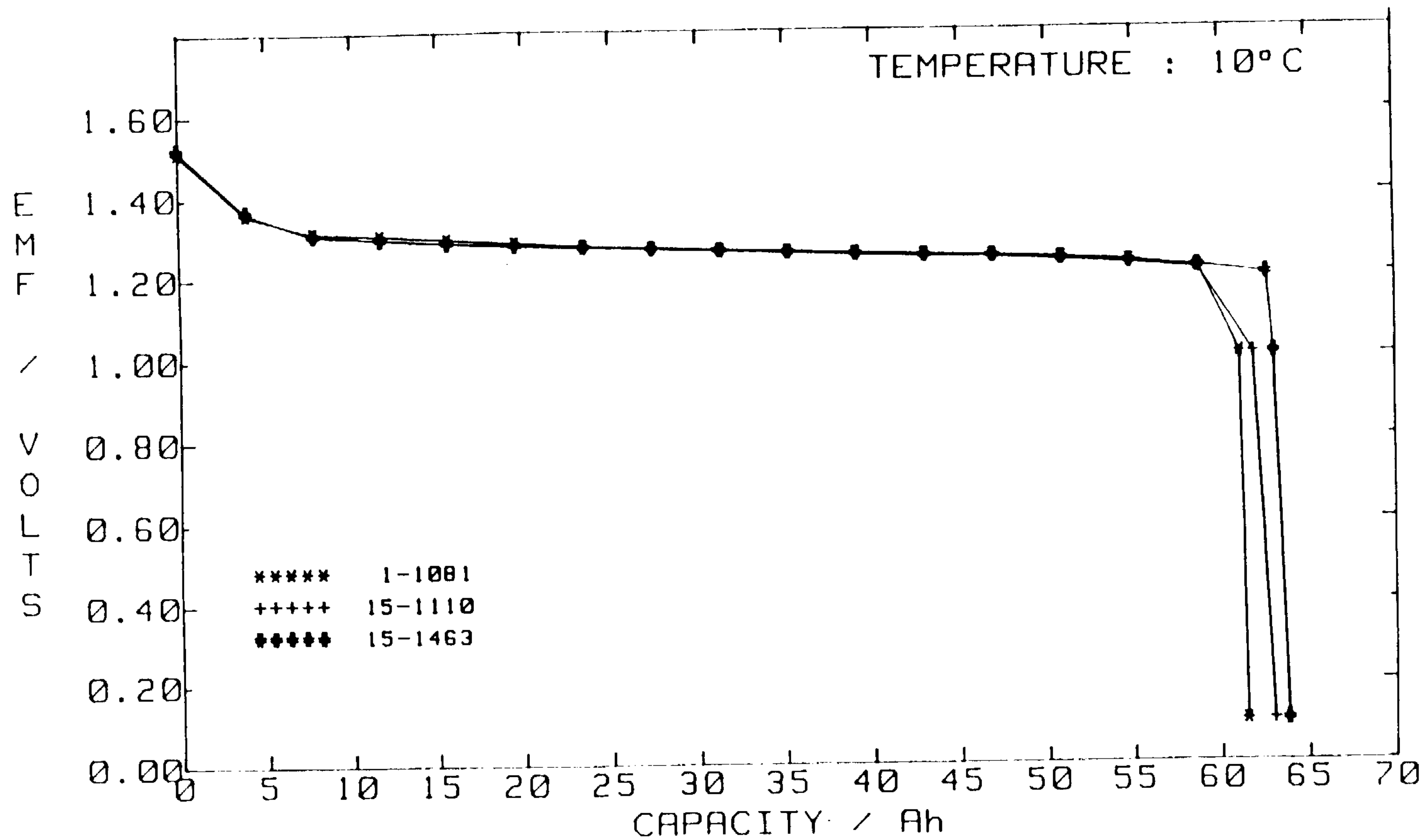
CAPACITY VARIATION WITH STORAGE



CAPACITY OF RTTC STORED CELLS



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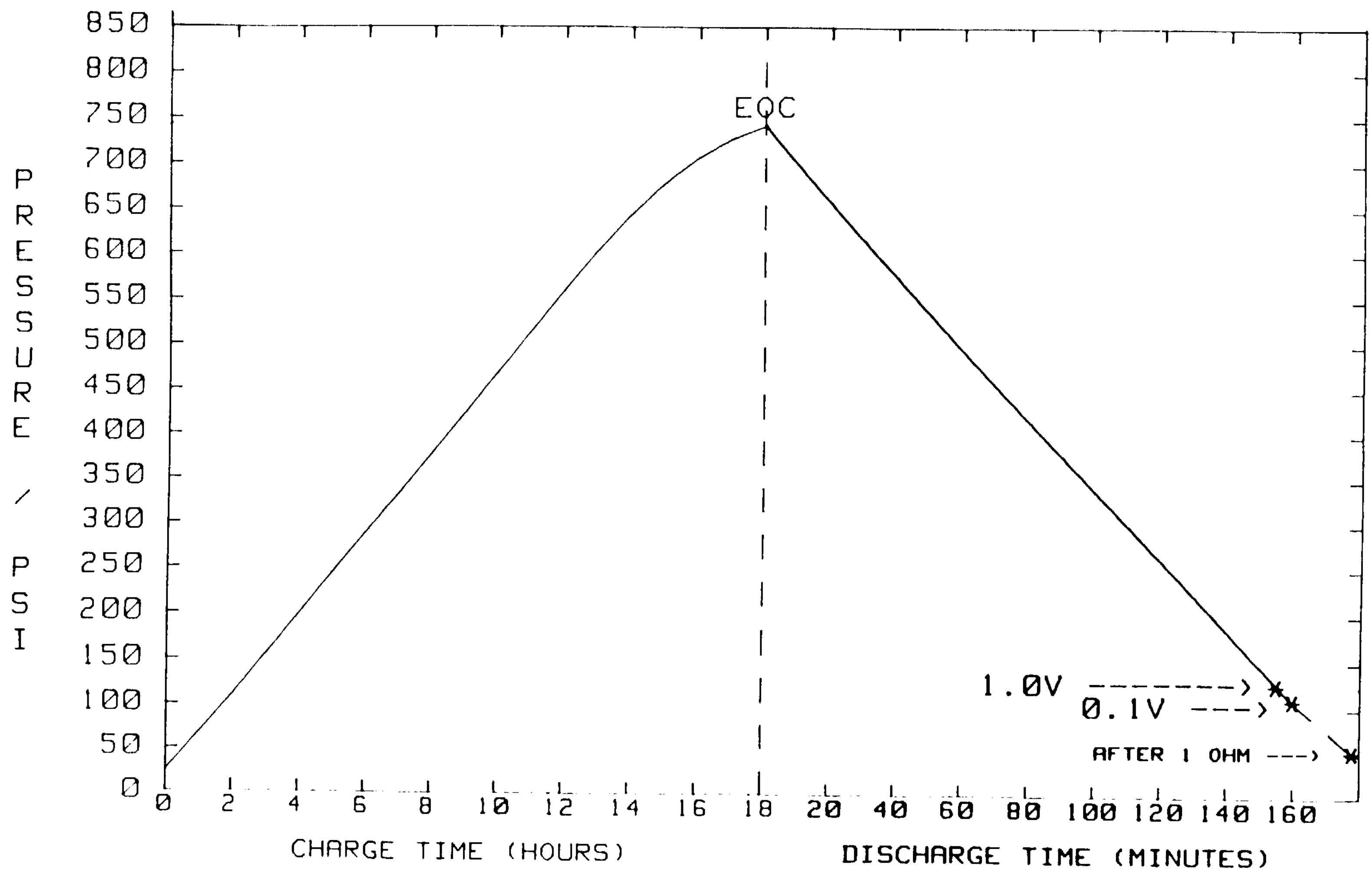
CHARGE/DISCHARGE DATA FOR S/N 15-1110 PRESSURE FROM RTTC STORED CELL



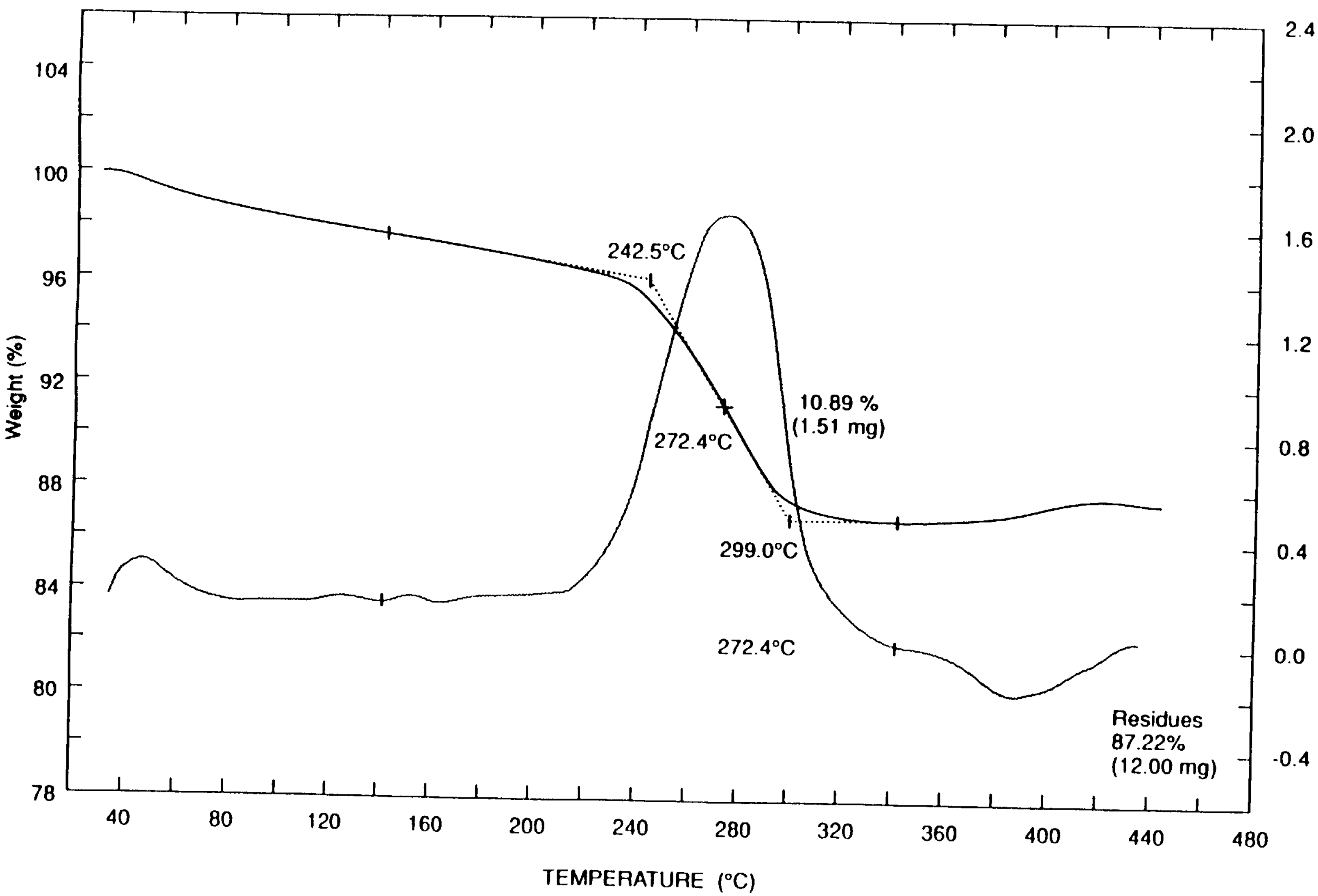
HYDRATION OF ACTIVE MATERIAL

- Literature data for molar ratio of Ni to H_2O in $Ni(OH)_2$ is between 1.1 to 2.36

- Three possible types of hydroxyl groups - interstitial water, water of crystallization and hydroxyl groups bonded to Ni atoms

- Exchange of water from the active material with the electrolyte is believed to be important in the redox reaction

TGA INTEGRAL AND DERIVATIVE PLOTS FOR ACTIVE MATERIAL FROM HAC/I-VI CELL S/N 074



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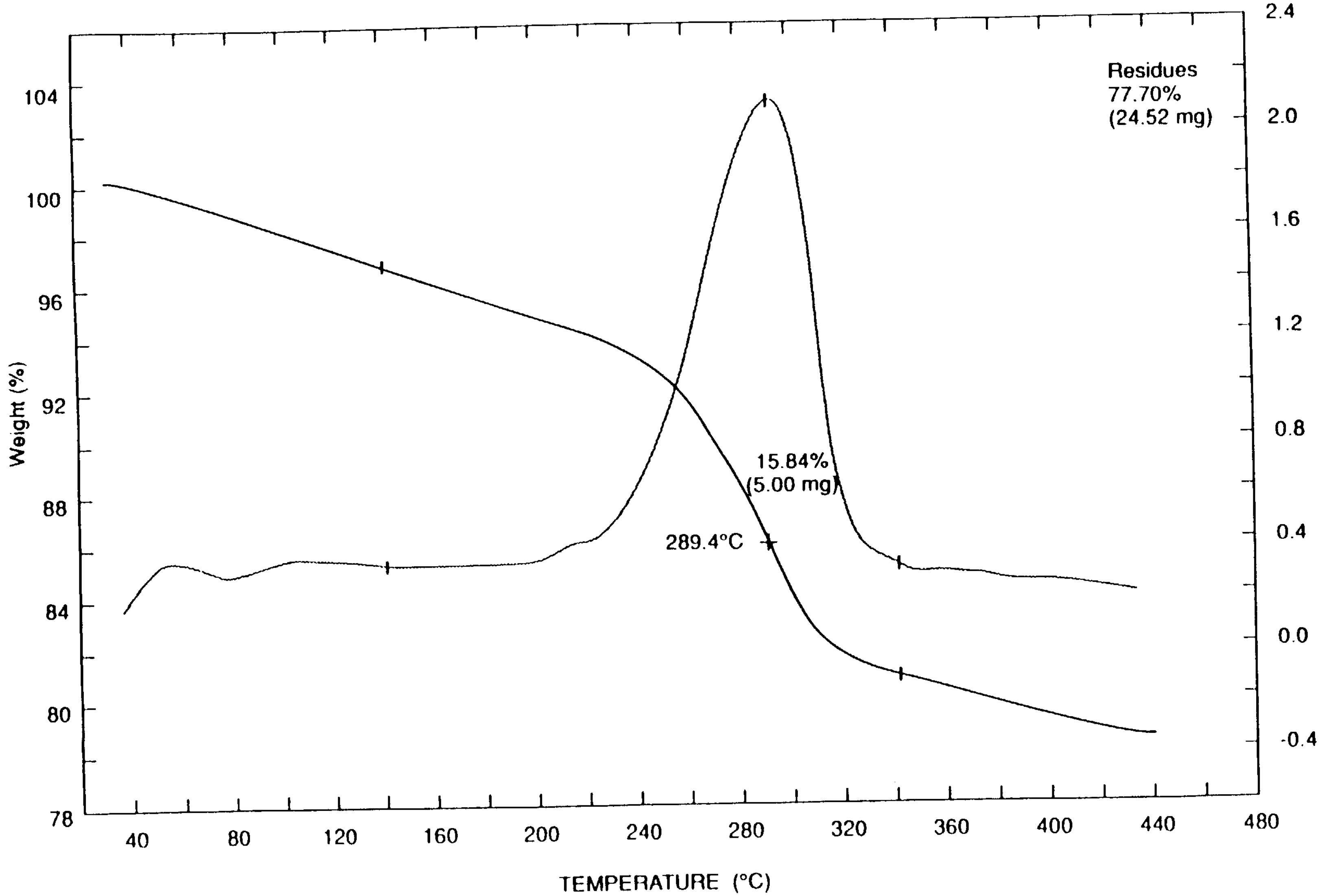
TGA INTEGRAL AND DERIVATIVE PLOTS FOR POSITIVE ACTIVE MATERIAL EP/I-V CELL S/N 06085



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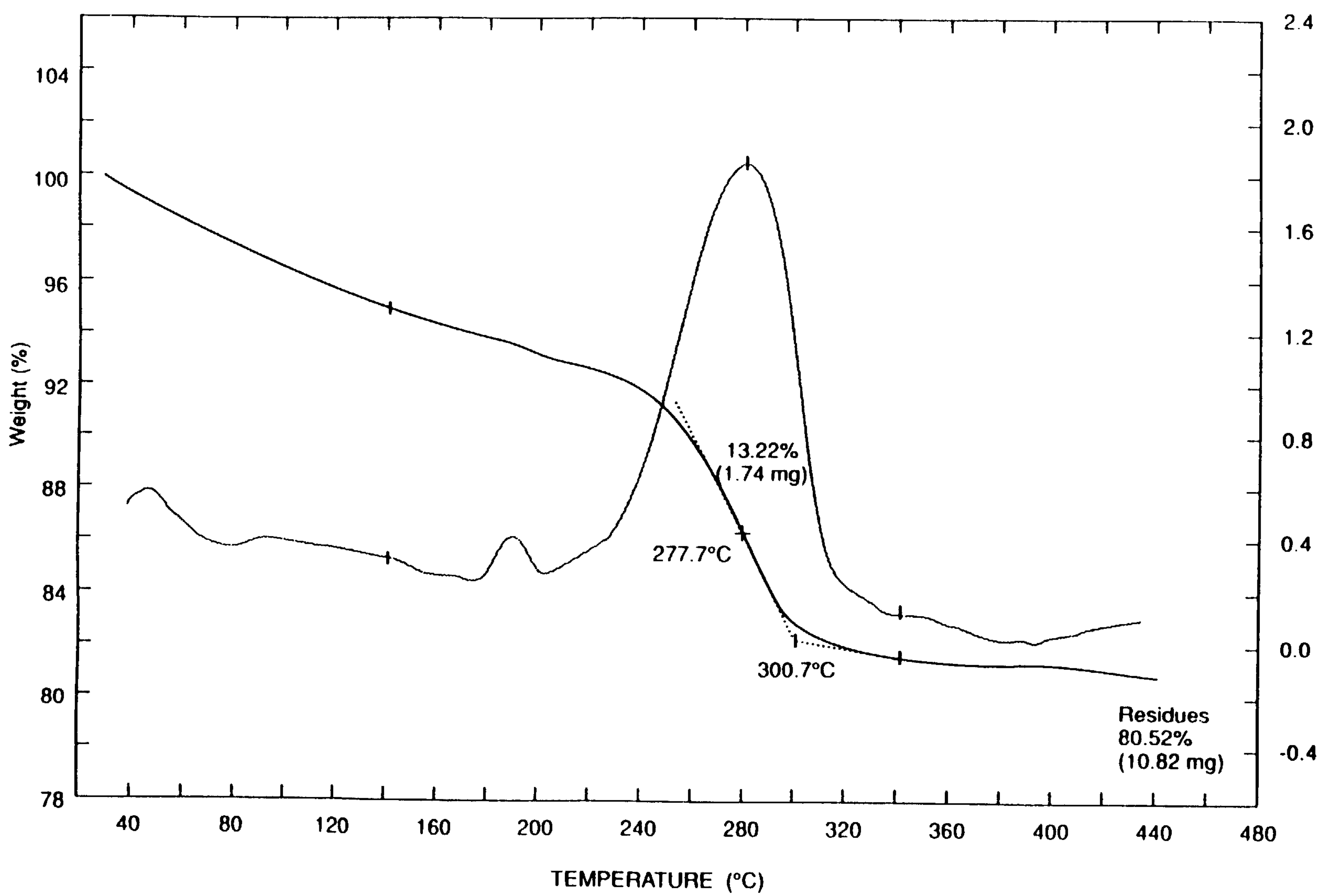
TGA INTEGRAL AND DERIVATIVE PLOTS FOR ACTIVE MATERIAL FROM HAC/I-VI CELL S/N 161



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WATER CONTENT FROM TGA

POSITIVE PLATE I.D.	WATER LOSS FROM 140-340°C OR WATER CONTENT (%)	PEAK TEMPERATURE (%)	COMMENTS
EP/INTELSAT V Cell S/N 06-085	15.84	289.4	Plate produced by aqueous electrochemical procedure. Did not exhibit capacity fading.
HAC/INTELSAT VI Virgin Plate 2087	13.71	253.9	Uncycled plate stored under N2 for 8 months.
HAC/INTELSAT VI	13.22	277.7	Exhibited capacity fading, but regained capacity upon conditioning.
HAC/INTELSAT VI S/N 074	10.89	272.4	Exhibited capacity fading. Did not regain capacity upon conditioning.

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HYDRATION OF ACTIVE MATERIAL

$$(Ni(OH)_2 \cdot x\,H_2O) \cdot y\,H_2O$$

- x and y cannot be determined since it is impossible to know the quantity of intercalated water removed before 150°C

- W. Dennstedt and W. Loser 1971

  S. Lebihan and M. Figlarz 1973

STRUCTUAL FORMULAE PROPOSED FOR THE ACTIVE MATERIAL *

CHARGED	DISCHARGED
$NiO(OH) \cdot 0.2\ H_2O$	$Ni(OH)_2$
$NiO(OH) \cdot H_2O$	$2Ni(OH)_2 \cdot 2H_2O$
$Ni_2O_3 \cdot 2H_2O$	$Ni(OH)_2 \cdot 0.34\ H_2O$
$Ni_2O_3 \cdot 3.21\ H_2O$	$2Ni(OH)_2 \cdot 1.28\ H_2O$
$Ni_3O_4 \cdot 2H_2O$	
$NiO(OH) \cdot 0.14\ KOH$	
$3NiO(OH) \cdot 7/2\ H_2O \cdot 3/4\ KOH$	
$kNiO_3O_6 \cdot 2H_2O$	

* Literature Data

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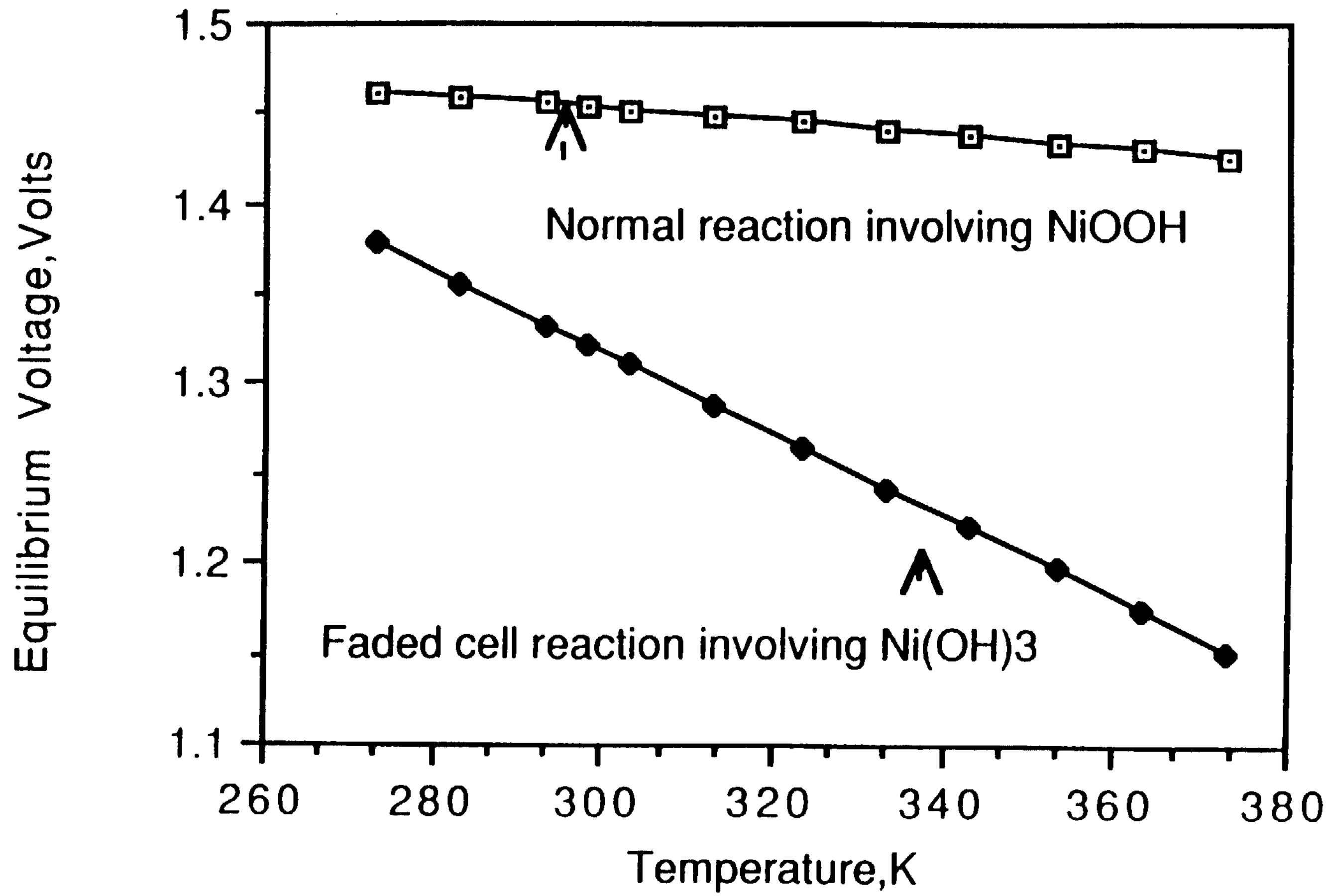
TEMPERATURE DEPENDENCY OF CALCULATED EMF *



* Data published by D. D. Macdonald and Mark L. Challingsworth in "Thermadynamics of Nickel-Cadmium and Nickel-Hydrogen Batteries"

MECHANISM FOR CAPACITY FADE

EXPERIMENTAL EVIDENCE

- The process is reversible since 95% of the capacity can be recovered
- Extremely low temperature maintains the capacity and sometimes helps in capacity recovery
- Techniques involving overcharging aid in capacity recovery
- Analysis of positive plates from faded cells indicated lower active material utilization
- Thermogravimetric analysis of plates from faded cells showed decreased water content
- The second plateau which appears is particularly prominent at high temperatures
- Low temperature cell capacity is lower in the cycle which immediately follows a 20-25°C capacity cycle

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PROPOSED MECHANISM

The capacity fade is due to the predominence of $Ni(OH)_3$ (alternately represented as NiOOH H_2O) in the positive active material. The reaction of the species produces an equilibrium potential which is not only lower but also very sensitive to increase in temperature. The interstitial water in this form of active material is less than that in the normal NiOOH structure.