JPL

# SODIUM - METAL CHLORIDE BATTERIES

PRECEDING PAGE BLANK NOT FILMED

JPL

B. V. RATNAKUMAR, A. I. ATTIA, G. HALPERT

N92-22768

OCTOBER 30, 1991
THE 1991 NASA AEROSPACE BATTERY WORKSHOP

BATTERY SYSTEMS GROUP

https://ntrs.nasa.gov/search.jsp?R=19920013525 2020-03-17T11:39:40+00:00Z

# OUTLINE

- CONFIGURATION AND ADVANTAGES
- CAPABILITIES OF THE SYSTEMS
- STUDIES AT JPL
- AREAS OF FURTHER STUDY

JPL

# SODIUM - METAL CHLORIDE BATTERIES

- CONFIGURATION

$$\text{Na (m) // Beta" ALUMINA // } NaAlCl_4\text{ (m) // } MCl_2\text{ (s)}$$

Na (m): Anode
Beta" ALUMINA: Solid Electrolyte Separator
$NaAlCl_4$ (m): Basic or Neutral
$MCl_2$ (s): Transition Metal Chloride

- CELL REACTION

$$2\,Na + MCl_2 \underset{ch}{\overset{disch}{\rightleftharpoons}} M + 2\,NaCl$$

- METAL CHLORIDES

FERROUS CHLORIDE
NICKEL CHLORIDE

- OPERATING TEMPERATURES : $\geq 250°C$

# COMPARISON WITH Na - S

## ADVANTAGES

- LOWER OPERATING TEMPERATURES (≥ 250°C)
- WIDER RANGE OF OPERATING TEMPERATURES ( 180 - 425°C)
- SAFETY IN THE EVENT OF INTERNAL SHORT AND TEMPERATURE EXCURSIONS
- FAILS SHORT CIRCUIT (NO NEED FOR BYPASS)
- BUILT-IN OVERCHARGE MECHANISM
- TOLERANCE TO OVERDISCHARGE
- ASSEMBLY IN THE DISCHARGED STATE WITH LITTLE OR NO SODIUM

## DISADVANTAGES

- MORPHOLOGICAL CHANGES AT THE CATHODE
- LOWER POWER DENSITIES

# CAPABILITIES OF THE SYSTEMS

## SUMMARY OF DEVELOPMENT IN THE U.K. / SOUTH AFRICA

- FERROUS CHLORIDE

  ENERGY DENSITIES OF 150 - 170 Wh/kg AT 2 - 4 h RATES WITH ELECTRODE POROSITIES ABOVE 80 % AND CONVERSION PERCENTAGES OF 30 - 40 %

  1000 CYCLES AND ONE YEAR OF OPERATION IN A 5 Ah CELL

  HIGH RATE DISCHARGE CAPABILITY IN AN 8 Ah CELL

  FLAT DISCHARGE CURVES (1.8 V) AT THE 1 h RATE (180 $mA/cm^2$ )

- NICKEL CHLORIDE

  2047 CYCLES IN A 7.5 Ah CELL WITH SULFUR ADDITIVE

  75 % OF THE ORIGINAL CAPACITY RETAINED AT THE 1 h RATE

  NO DEGRADATION OF BETA ALUMINA

  NO LOSS IN THE SINTERED STRUCTURE OF THE ELECTRODE

JPL

# CAPABILITIES OF THE SYSTEMS

## PERFORMANCE OF $MCl_2$ CELLS AND BATTERIES

| PARAMETER → / TYPE ↓ | | CAPACITY Amp. Hr | PRACTICAL ENERGY DENSITY @ 5 hr RATE | | SPECIFIC POWER @2/3 OCV AND 70%DOD W / Kg |
|---|---|---|---|---|---|
| | | | Wh / Kg | Wh / l | |
| BETA 33 CELL ·33 mm dia and 160-200 mm long | $FeCl_2$ | 42 | 142 | 260 | 139 |
| | $NiCl_2$ | 40 | 124 | 310 | 150 |
| BETA 55 CELL 55 dia and 230-300 mm long | $FeCl_2$ | 140 | 110 | 172 | - |
| | $NiCl_2$ | 100 | 109 | 155 | - |
| BETA 55 BATTERY | $FeCl_2$ | 15 KWh | 88 | 103 | - |
| | $NiCl_2$ | 30 KWh | 88 | 95 | - |

A. R. Tilley and R. N. Bull, 22nd IECEC; 1078 (1987)

JPL

# ENVIRONMENTAL TESTS ON Na/$MCl_2$ CELLS

- CRUSHING : NO CELL BREACHING; TEMP. RISE OF 75°C
- SHORT CIRCUIT :
  - INTERNAL : TEMPERATURE RISE TO 500°C
  - EXTERNAL : NO EFFECT
- OVERHEATING TO 750°C : NO CELL BREACHING; SLIGHT LEAKAGE
- FREEZE-THAW CYCLING : NO FAILURE AFTER 50 CYCLES
- OVERCHARGE : NO EFFECT (SLIGHT LEAKAGE ABOVE > 100%)
- OVERDISCHARGE : NO EFFECT
- SHOCK AND VIBRATION : NO FAILURE IN BOTH FIXED AMPLITUDE AND VEHICLE SIMULATION TESTS

R. J. WEDLAKE AND A. R. TILLEY, B. ELECTROCHEM., 4, 41 (1988)

JPL

# Na / $NiCl_2$ CELLS FOR SPACE APPLICATIONS AT ESTEC

- FEASIBILITY STUDIES : 100 - 120 Wh/Kg
  PROTOTYPE CELLS : 59 - 70 Wh/Kg

- AFTER 2810 GEO AND LEO CYCLES
  - NO DEGRADATION FOR BETA ALUMINA
  - RECHARGE RATIO ~ UNITY
  - ROUND TRIP ENERGY EFFICIENCY HIGH
  - CAPACITY DECLINED BY 40 %.

- NEED FOR CELL OPTIMIZATION
  - ELECTRODE THICKNESS
  - ALTERNATE ELECTROLYTE GEOMETRIES

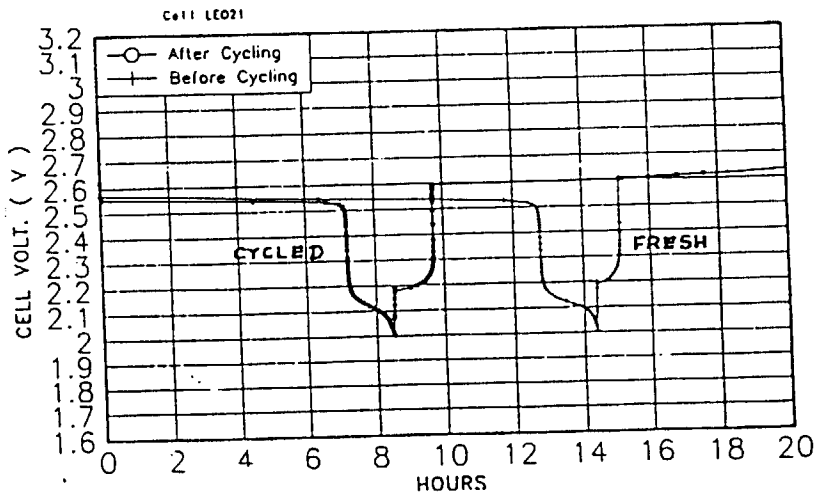



Fig. 8 CELL CAPACITY AT 1 A RATE BEFORE & AFTER 2810 CYCLES

B. Hendel and G. DUDLEY, NASA Workshop, December 1990

# JPL EFFORT

## OBJECTIVE

- TO DEVELOP A HIGH SPECIFIC ENERGY BATTERY FOR FUTURE NASA MISSIONS

## APPROACH

- TO IDENTIFY , EVALUATE AND DEVELOP ALTERNATE CATHODE MATERIALS TO SULFUR FOR RECHARGEABLE SODIUM BATTERIES

### INITIAL STUDIES

- ORGANIC CATHODE MATERIALS

  EVALUATED TCNE AND TCNQ AS POSSIBLE ALTERNATIVES

  PROBLEMS OF THERMAL INSTABILITY, POLYMERIZATION LIKELY

- INORGANIC CATHODE MATERIALS

  TRANSITION METAL CHLORIDES IN CHLOROALUMINATE MELTS

# JPL EFFORT - PRESENT APPROACH

## METAL CHLORIDE CATHODES

- FUNDAMENTAL STUDIES IN SINGLE ELECTRODE CONFIGURATION TO
  - ESTABLISH THE MECHANISMS FOR THE REDUCTION OF $FeCl_2$ AND $NiCl_2$
  - PREDICT THE FEASIBILITY OF USING OTHER TRANSITION METAL CHLORIDES
  - IDENTIFY RATE-LIMITING PROCESSES
  - DETERMINE THE ELECTRODE KINETICS
  - STUDY THE EFFECTS OF ADDITIVES
- PERFORMANCE EVALUATION IN LABORATORY TEST CELLS
- IDENTIFY THE FAILURE MODES

# MECHANISM OF $FeCl_2$ REDUCTION

- EVIDENCE FOR TWO - STEP REACTION MECHANISM FROM CYCLIC VOLTAMMETRY

  $Na_6FeCl_8$ INTERMEDIATE

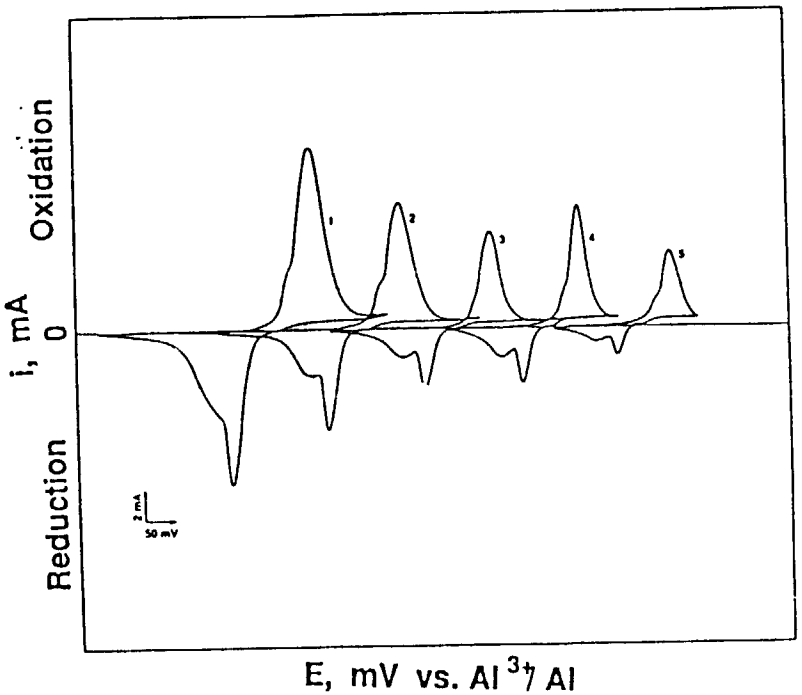
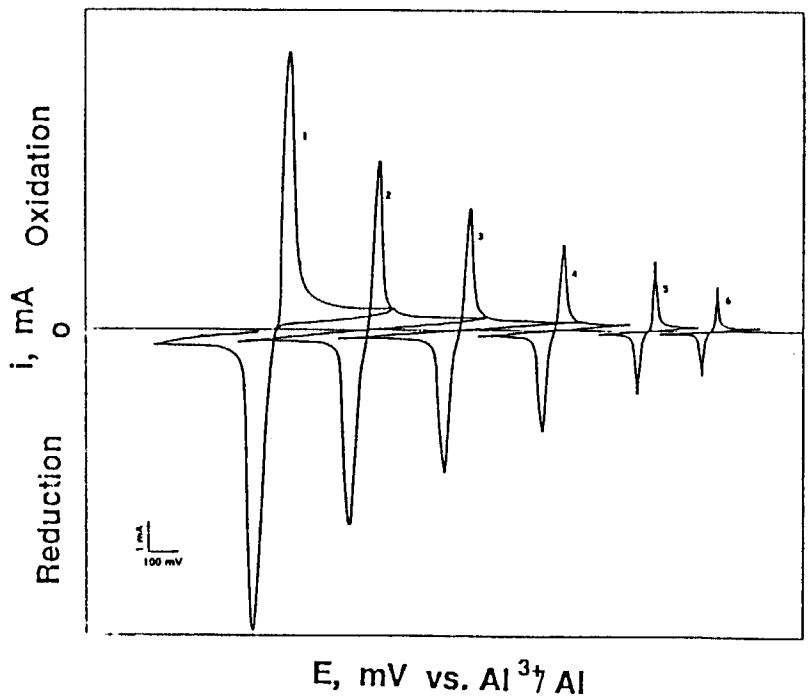



Fig. 3. Cyclic voltammograms of Fe electrode (area: 0.05 $cm^2$) in $NaAlCl_4$ at 220°C at scan rates of 1.) 20, 2.) 10, 3.) 5, 4.) 2, and 5.) 1 mV/s. Scale on the y axis is 1 mA/cm (reduced to half) for curves 4 and 5.

- Ni ADDITIONS FOR OVERCHARGE PROTECTION OF $FeCl_2$

# MECHANISM OF $NiCl_2$ REDUCTION

- SINGLE - STEP REACTION SCHEME CONFIRMED BY CYCLIC VOLTAMMETRY




Cyclic voltammetric curves of Ni electrode in $NaAlCl_4$ at 220°C at different scan rates of 1) 50, 2) 20, 3) 10, 4) 5, 5) 2 and 6) 1 mV/s.

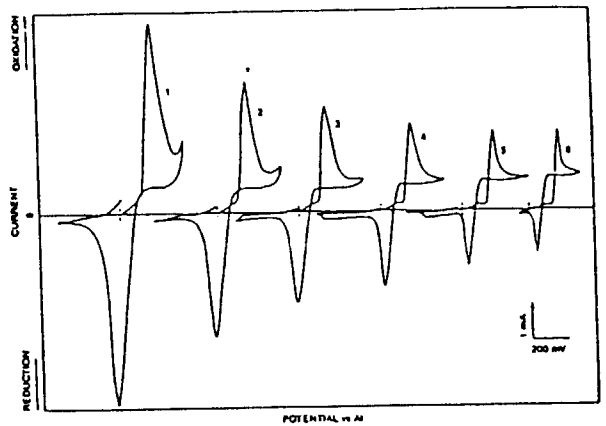
- GOOD REVERSIBILITY

JPL

# OTHER METAL CHLORIDES

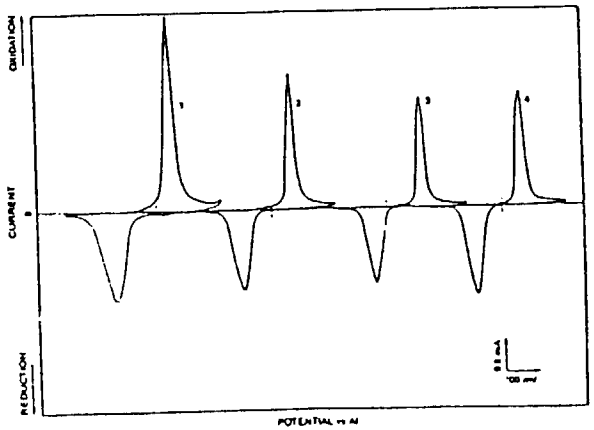
- REQUIRED CRITERIA FROM CYCLIC VOLTAMMETRY
  - ..Low oxidation currents subsequent to peak indicate low solubility for the chloride
  - .. Reversible peaks and single step
- Ti, V, Mn, Cr, Al and Ag UNLIKELY.
  - .. High oxidation currents.
- COPPER EXHIBITS TWO - STEP OXIDATION (SECOND STEP FORMS SOLUBLE CHLORIDE)
  - .. Unlikely.
- COBALT AND MOLYBDENUM ARE LIKELY CATHODE MATERIALS
  - .. Low oxidation currents.
- MOLYBDENUM IS A STABLE CURRENT COLLECTOR FOR $NiCl_2$.

Co



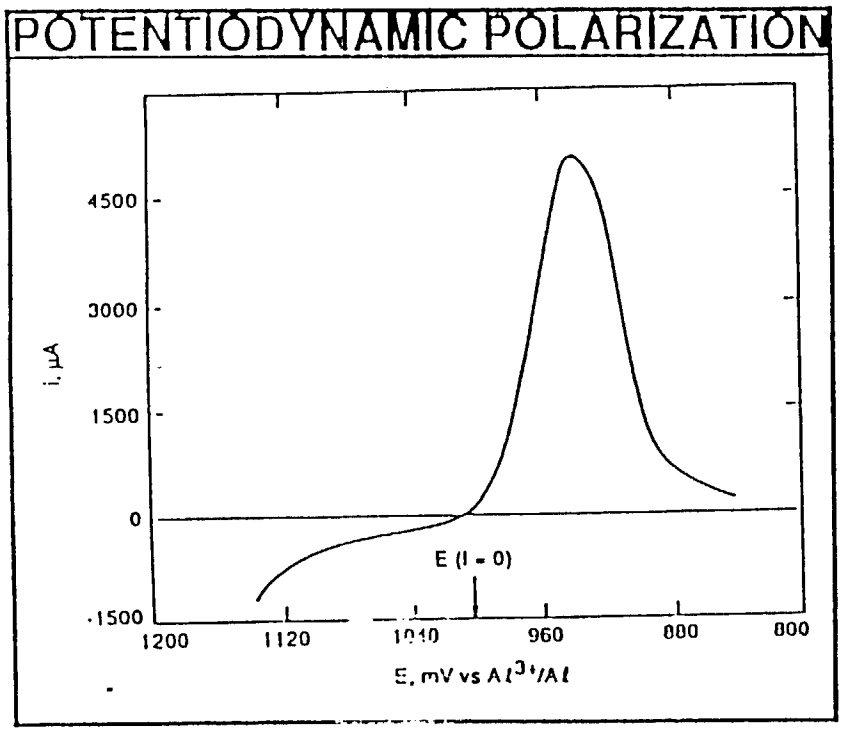

Voltammograms of Co ($E_o$:870 mV) at 1) 50, 2) 20, 3) 10, 4) 5, 5) 2 and 6) 1 mV/s.

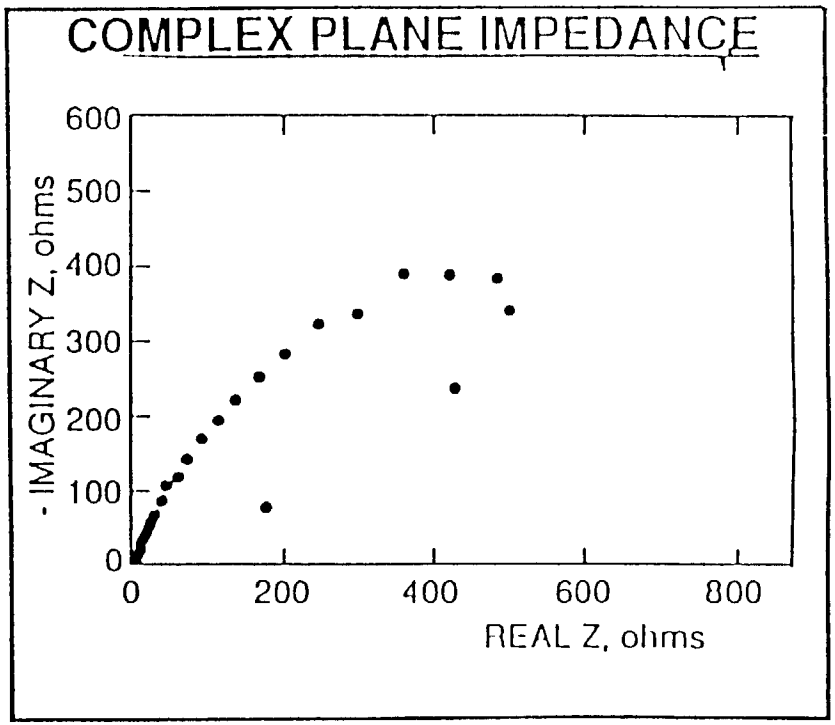
Mo




Voltammograms of Mo ($E_o$:997 mV) at 1) 50, 2) 20, 3) 10 and 4) 5 mV/s (Scale on Y-axis doubled for curve 4).

# PASSIVATION OF $NiCl_2$

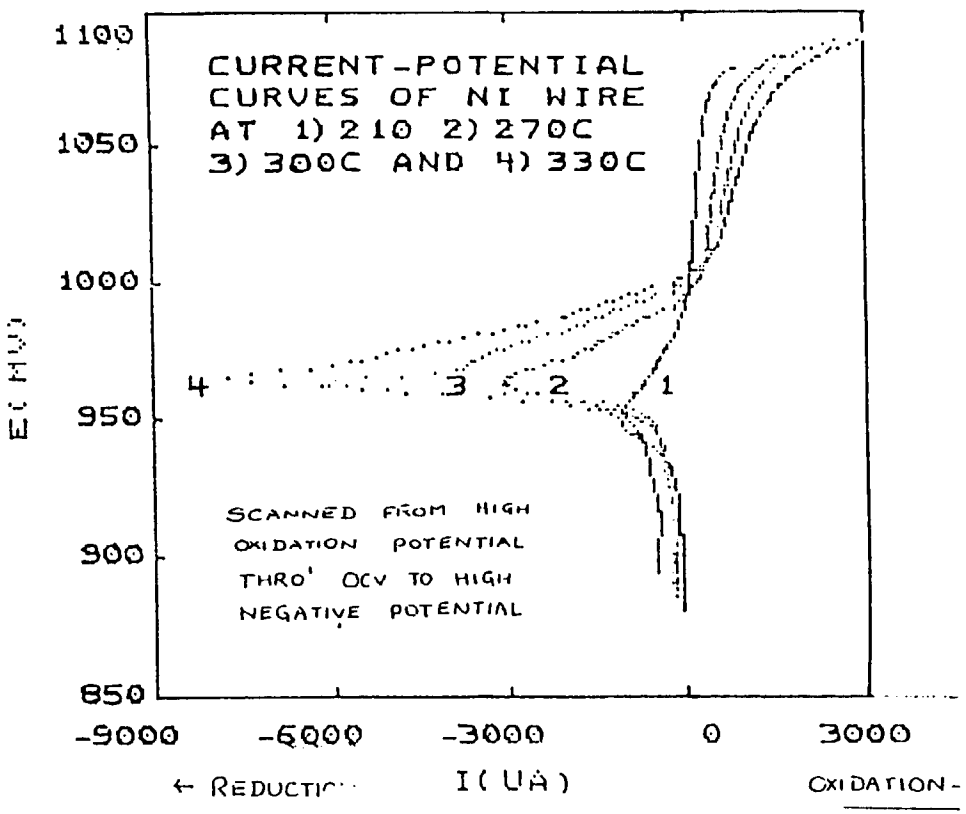



- PASSIVATION DURING REDUCTION BY NaCl PRECIPITATION
- PASSIVATION MORE PROMINENT THAN IN $FeCl_2$

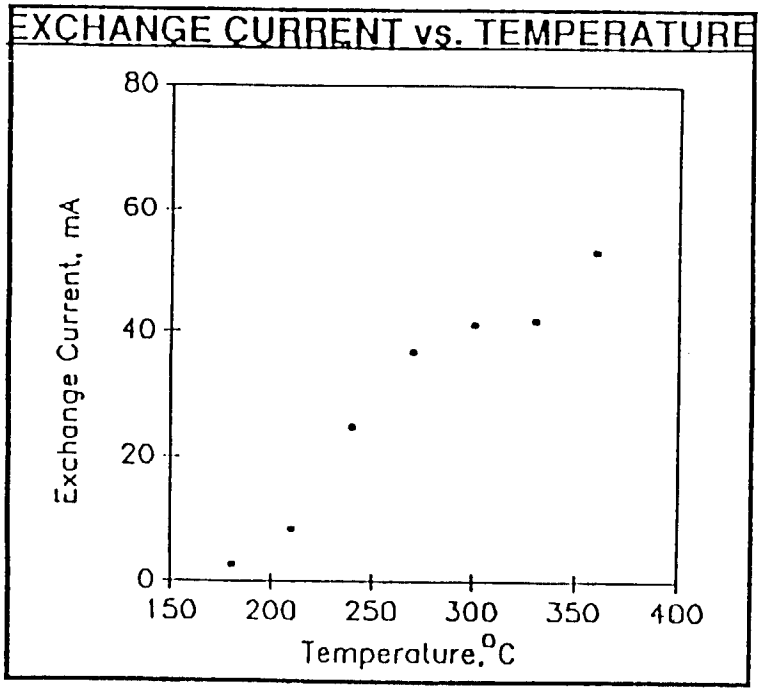
# PASSIVATION OF $NiCl_2$

- PASSIVATION INCREASES AT LOWER STATES OF CHARGE AND LOWER ELECTRODE POTENTIALS.
- PASSIVATION IS ALLEVIATED BY INCREASING THE PORE SIZE OF THE ELECTRODE
- PASSIVATION CAN BE REDUCED BY OPERATING AT HIGHER TEMPERATURES



# KINETICS OF $MCl_2$ REDUCTION

- HIGH EXCHANGE CURRENT DENSITIES (1 $mA/cm^2$) FOR BOTH $FeCl_2$ AND $NiCl_2$.
- 10 % INCREASE IN THE EXCHANGE CURRENT DENSITY OF $NiCl_2$ FOR EACH 10°C RISE IN THE OPERATING TEMPERATURE.
- OPTIMUM TEMPERATURE FOR $NiCl_2 \geq$ 250°C.



# ADDITIVE REQUIRED FOR $NiCl_2$

- DECLINE IN CAPACITY PREMATURELY

  EFFECT MORE PROMINENT AT HIGHER POROSITIES
- LOSS OF SINTERED STRUCTURE DUE TO AN AGGLOMERATION OF Ni PARTICLES

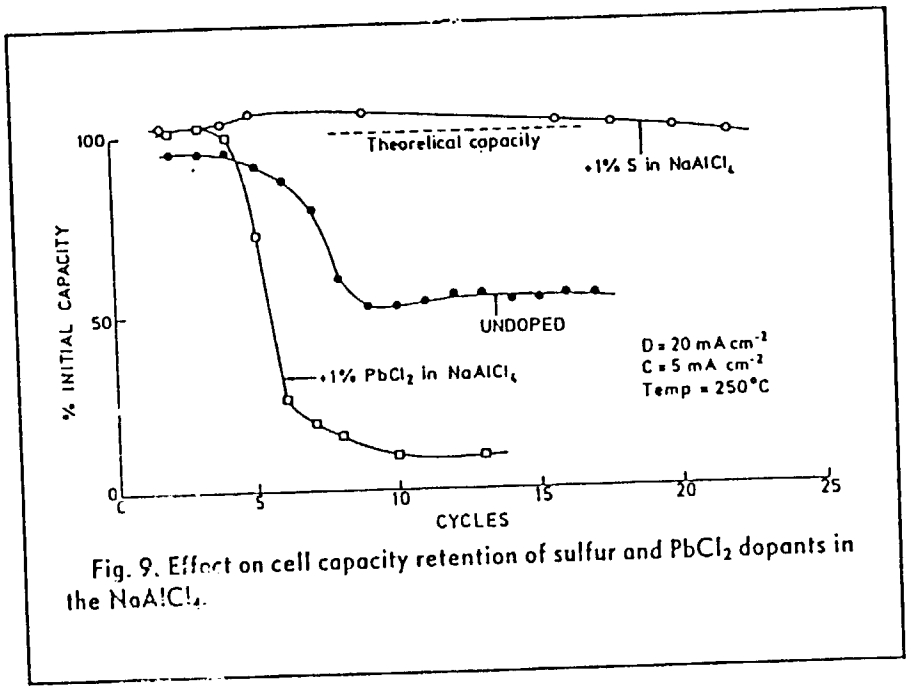



Fig. 9. Effect on cell capacity retention of sulfur and $PbCl_2$ dopants in the $NaAlCl_4$.

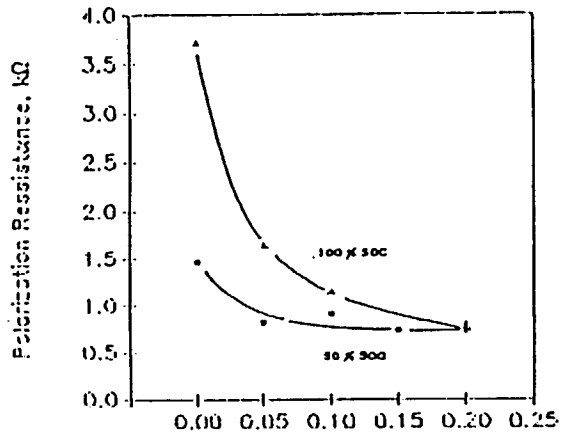
R. J. Bones, D. A. Teagle, S. D. Brooker and F. L. cullen
J. Electrochem., Soc., 136, 1274 (1989).

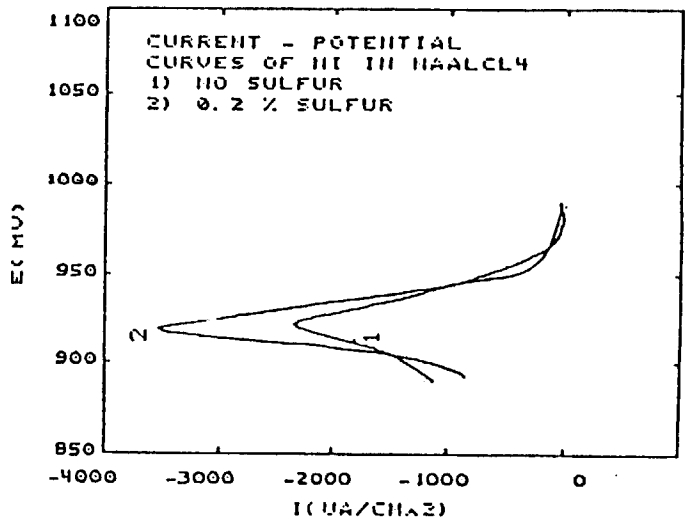
- SULFUR REDUCES MORPHOLOGICAL CHANGE

JPL

# EFFECT OF SULFUR ON $NiCl_2$ KINETICS

- HIGHER PEAK CURRENTS IN CYCLIC VOLTAMMETRIC CURVES
- IMPROVEMENT IN RECHARGEABILITY
- ENHANCED KINETICS OF $NiCl_2$ REDUCTION
- REDUCED PASSIVATION
- MAXIMUM SULFUR CONTENT ~0.2 w% IN THE ELECTROLYTE

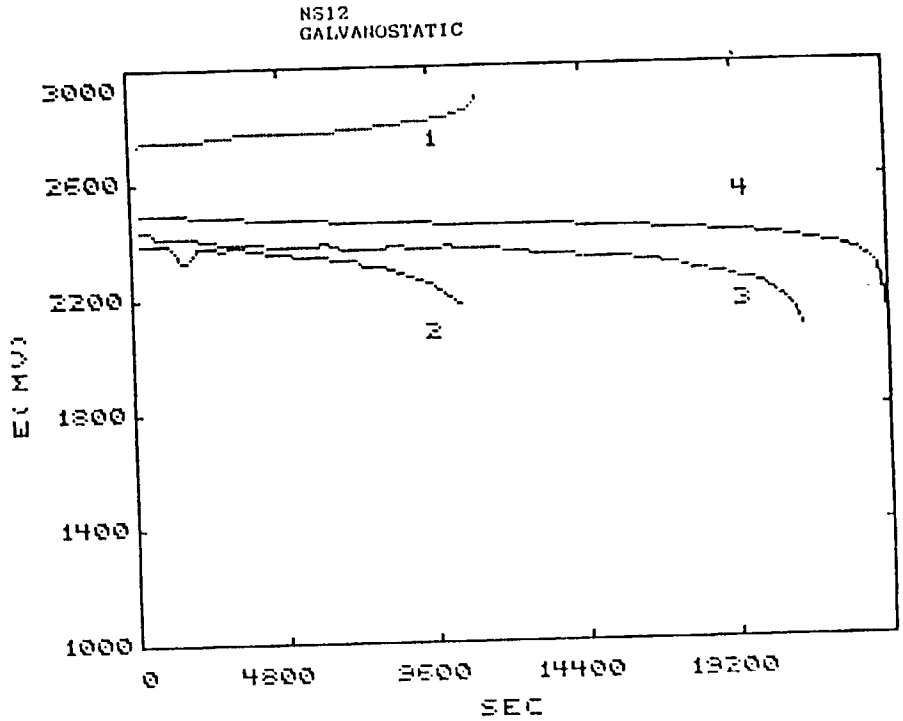


JPL

# PRELIMINARY PERFORMANCE DATA OF 1 Ah CELL

- HIGH ROUND TRIP EFFICIENCY (~ 95%)
- 50 % CONVERSION OF NaCl
- HIGH DISCHARGE YIELDS OF ABOVE 80 % AT THE 4 - 5 h RATES
- FORMATION APPEARS TO BE INCOMPLETE AND REQUIRES OPTIMIZATION




DISCHARGE CURVES OF 1 Ah Na /$NiCl_2$ CELL AT 75 mA (7.5 mA/$cm^2$ ) AND AT 250°C

1) FIFTH CHARGE AT 75 mA
2) FIFTH DISCHARGE
3) SIXTH DISCH. AFTER CHARGE AT 30 mA
4) SEVENTH DISCH. AFTER CHARGE AT 20 mA

# FABRICATION PARAMETERS VS. ENERGY DENSITY

- OPTIMIZE CONVERSION EFFICIENCY (RATIO OF NaCl : M) AND ELECTRODE POROSITY

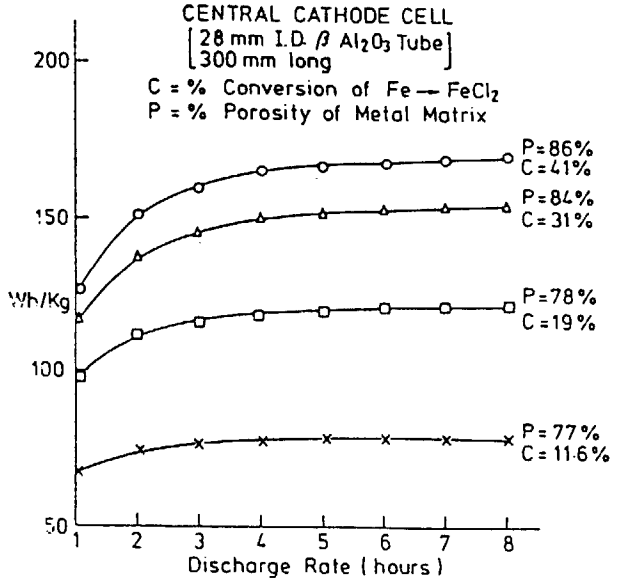



Fig. 5. Cell energy density at various discharge rates (each at optimum cathode thickness).

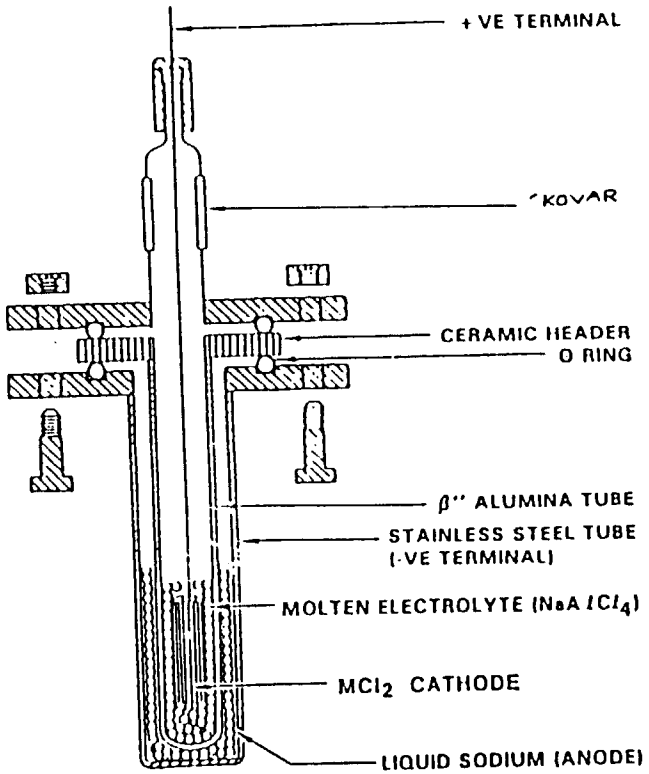
R. J. Bones, J. Coetzer, R. C. Galloway and D. A. Teagle, J. Electrochem., Soc., 134, 2379 (1987).

- STATE OF THE ART ELECTRODES:

  33 % CONVERSION AND 90 % POROSITY

# 5 Ah CELL AS TEST VEHICLE

- CYLINDRICAL CENTRAL CATHODE,; CATHODE - LIMITED DESIGN (Na : ~ 200 - 300%)
- BETA ALUMINA TUBES WITH ALPHA ALUMINA HEADER
- MECHANICAL COMPRESSION SEAL
- KOVAR TO GLASS SEAL FOR CATHODE



# AREAS OF STUDY

- IMPROVEMENT IN POWER DENSITIES
  - ALTERNATE ELECTRODE DESIGNS
    - OTHER METHODS OF ELECTRODE FABRICATION
  - ALTERNATE ELECTROLYTE GEOMETRIES
    - FLAT PLATE BETA WITH POSSIBLY Na ALLOYS
- IMPROVEMENT IN CYCLE LIFE
  - NON-SULFUR ADDITIVES FOR MORPHOLOGICAL BENEFITS
    - ELECTRODE FABRICATION
    - CELL DESIGN FOR SCREENING OF ADDITIVES
- DESIGN OPTIMIZATION FOR HIGH SPECIFIC ENERGIES
  - CELL / BATTERY DESIGN
    - SEALING METHODS
    - COMPONENTS RATIO
    - CELL CONFIGURATION
- RELIABILITY
  - FAILURE ANALYSIS

JPL

# SODIUM- METAL HALIDE CELL PROGRAM

| ACTIVITY | 88 89 90 91 92 93 94 95 96 97 98 99 2000 | |
|---|---|---|
| SCREENING STUDIES | Evaluate organic and inorganic cathodes<br>Down select to Na/MCl2 | IDENTIFY SYSTEM CAPABLE OF PROVIDING > 1000 CYCLES AND 150 Wh/Kg |
| ELECTROCHEMICAL CHARACTERIZATION OF MCl2 | Short term studies performance and reversibility<br>Identify suitable materials<br>Identify and overcome rate limiting processes<br>Down select to Na/NiCl2 | ESTABLISH MECHANISMS DETERMINE REACTION KINETICS AND IDENTIFY RATE LIMITING PROCESSES |
| COMPONENT DEVELOPMENT | Develop 5 Ah TEST CELL<br>Study of performing enhancing additives<br>Develop cathode fabication process<br>Identify cell failure mechanism<br>Charge methods<br>Optimize and improve design | DEFINE DESIGN REQUIREMENTS FOR 20-25 Ah CELLS |
| PERFORMANCE AND SAFETY EVALUATION | Develop performance data base<br>Evaluate safety and environmental effects<br>Identify failure modes | DEMONSTRATE CYCLE LIFE AND PERFORMANCE IN OPTIMIZED 20-25 Ah CELL |
| PROTO TYPE | Develop eng model cell<br>Demo 1000 cycles and 150 Wh/Kg | FINAL DEMONSTRATION |

JPL

# PUBLICATIONS FROM JPL ACTIVITIES

1. "AEROSPACE APPLICATIONS OF SODIUM BATTERIES USING NOVEL CATHODE MATERIALS",
PROC. OF 24th IECEC, WASINGTON D.C., AUG. 1989.

2. "ORGANIC CATHODE MATERIALS IN SODIUM BATTERIES"
J. APPLIED ELECTROCHEMISTRY, 20 , 357 - 364 (1990).

3. "ADVANCED RECHARGEABLE SODIUM BATTERIES WITH NOVEL CATHODES"
J. POWER SOURCES, 29, 301 - 309 (1990).

4. "ELECTROCHEMISTRY OF METAL CHLORIDES IN SODIUM BATTERIES".
J. ELECTROCHEM. SOC., 137, 2991 - 2997 (1990).

5. "ALTERNATE CATHODES FOR SODIUM - METAL CHLORIDE BATTERIES"
J. ELECTROCHEM. SOC., 138, 883 -884 (1991).

6. "SODIUM - METAL CHLORIDE BATTERY RESEARCH AT JPL"
PROC. SERT CONF., APRIL 1991.

7. "PROGRESS AND RECENT DEVELOPMENTS IN SODIUM - METAL CHLORIDE BATTERIES"
PROC. 26th IECEC, BOSTON, MA, AUG. 1991.

# CONCLUSIONS

- RAPID DEVELOPMENT IN THE TECHNOLOGY OF Na / $MCl_2$ BATTERIES HAS BEEN ACHIEVED IN THE LAST DECADE MAINLY DUE TO THE :
  - .. EXPERTISE AVAILABLE WITH Na / S SYSTEM
  - .. SAFETY AND
  - .. FLEXIBILITY IN DESIGN AND FABRICATION

- LONG CYCLE LIVES OF OVER 1000 AND HIGH ENERGY DENSITIES OF ~ 100 Wh/Kg HAVE BEEN DEMONSTRATED IN BOTH Na / $FeCl_2$ AND Na / $NiCl_2$ CELLS.

- OPTIMIZATION OF POROUS CATHODE AND SOLID ELECTROLYTE GEOMETRIES ARE ESSENTIAL FOR FURTHER ENHANCING THE PERFORMANCE.

- FUNDAMENTAL STUDIES CONFIRM THE CAPABILITIES OF THESE SYSTEMS. $NiCl_2$ EMERGES AS THE CANDIDATE CATHODE MATERIAL FOR HIGH POWER DENSITY APPLICATIONS SUCH AS ELECTRIC VEHICLE AND SPACE.