SODIUM - METAL CHLORIDE BATTERIES

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

OCTOBER 30, 1991
THE 1991 NASA AEROSPACE BATTERY WORKSHOP
SODIUM - METAL CHLORIDE BATTERIES

- CONFIGURATION

\[
\text{Na (m) // Beta'' ALUMINA // NaAlCl}_4 (m) // \text{MCl}_2 (s)
\]

Anode Solid Electrolyte Basic or Transition Metal Chloride Separator Neutral

- CELL REACTION

\[
disch \quad 2 \text{Na} + \text{MCl}_2 \rightleftharpoons \text{M} + 2 \text{NaCl}
\]

ch

- METAL CHLORIDES

FERROUS CHLORIDE
NICKEL CHLORIDE

- OPERATING TEMPERATURES: \( \geq 250^\circ\text{C} \)
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/cm²)

- **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

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BATTERY SYSTEMS GROUP
### CAPABILITIES OF THE SYSTEMS

#### PERFORMANCE OF MCl₂ CELLS AND BATTERIES

<table>
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<tr>
<th>PARAMETER</th>
<th>CAPACITY</th>
<th>PRACTICAL ENERGY DENSITY @ 5 hr RATE</th>
<th>SPECIFIC POWER @2/3 OCV AND 70%DOD</th>
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<td>TYPE</td>
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<td>Wh / Kg</td>
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<td>BETA 33 CELL</td>
<td>FeCl₂</td>
<td>42</td>
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<td>NiCl₂</td>
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<td>33 mm dia and 160-200 mm long</td>
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<td>BETA 55 CELL</td>
<td>FeCl₂</td>
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<td>NiCl₂</td>
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<td>55 dia and 230-300 mm long</td>
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<td>BETA 55 BATTERY</td>
<td>FeCl₂</td>
<td>15 KWh</td>
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<td>NiCl₂</td>
<td>30 KWh</td>
<td>88</td>
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A. R. Tilley and R. N. Bull, 22nd IECEC; 1078 (1987)
ENVIRONMENTAL TESTS ON Na/MCl₂ 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%)

- OVERD'SCHARGE: NO EFFECT

- SHOCK AND VIBRATION: NO FAILURE IN BOTH FIXED AMPLITUDE AND VEHICLE SIMULATION TESTS

Na / NiCl₂ 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

BATTERY SYSTEMS GROUP
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 CLOROALUMINATE MELTS

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JPL EFFORT - PRESENT APPROACH

METAL CHLORIDE CATHODES

- FUNDAMENTAL STUDIES IN SINGLE ELECTRODE CONFIGURATION TO ESTABLISH THE MECHANISMS FOR THE REDUCTION OF FeCl₂ AND NiCl₂

- 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 FeCl₂ REDUCTION

EVIDENCE FOR TWO-STEP REACTION MECHANISM FROM CYCLIC VOLTAMMETRY

Na₆FeCl₈, INTERMEDIATE

Fig. 3. Cyclic voltammograms of Fe electrode (area: 0.05 cm²) in NaClO₄ at 22°C at scan rates of 10, 20, 30, 50, 100, and 500 mV/s. Scale on the y-axis is 1 mA/cm (reduced to half) for curves 1 and 2.

E, mV vs. Al₃⁺/Al
MECHANISM OF NiCl₂ REDUCTION

- SINGLE-STEP REACTION SCHEME CONFIRMED BY CYCLIC VOLTAMMETRY

Cyclic voltammetric curves of Ni electrode in NaAlCl₄ 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
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, A1 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 NiCl₂.

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

Voltammograms of Mo (Eₒ: 997 mV) at 1) 50, 2) 20, 3) 10 and 4) 5 mV/s (Scale on Y-axis doubled for curve 4).
PASSIVATION OF NiCl₂

- PASSIVATION DURING REDUCTION BY NaCl PRECIPITATION
- PASSIVATION MORE PROMINENT THAN IN FeCl₂
PASSIVATION OF NiCl₂

- 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

CURRENT-POTENTIAL CURVES OF Ni WIRE AT 1) 210°C 2) 270°C 3) 300°C AND 4) 330°C

SCANNED FROM HIGH OXIDATION POTENTIAL THRO' OCV TO HIGH NEGATIVE POTENTIAL

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KINETICS OF MCI$_2$ 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$_2$ ≥ 250°C.
ADDITIVE REQUIRED FOR $\text{NiCl}_2$

- 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 $\text{PbCl}_2$ dopants in the $\text{NaAlCl}_4$.

R. J. Bones, D. A. Teagle, S. D. Brooker and F. L. Cullen

- SULFUR REDUCES MORPHOLOGICAL CHANGE
EFFECT OF SULFUR ON NiCl₂ KINETICS

- HIGHER PEAK CURRENTS IN CYCLIC VOLTAMMETRIC CURVES
- IMPROVEMENT IN RECHARGEABILITY
- ENHANCED KINETICS OF NiCl₂ REDUCTION
- REDUCED PASSIVATION
- MAXIMUM SULFUR CONTENT ~0.2 w% IN THE ELECTROLYTE
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/NaCl$_2$ 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

![Diagram showing energy density vs. discharge rate]

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

- 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

BATTERY SYSTEMS GROUP
# Sodium-Metal Halide Cell Program

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**Note:** The diagram and table outline the activities and timelines for the Sodium-Metal Halide Cell Program, focusing on key milestones such as system identification, chemical characterization, component development, performance evaluation, and prototype development. The program aims to develop a system capable of providing over 1000 cycles with a capacity of 150 Wh/Kg, with a focus on identifying and overcoming rate-limiting processes and determining reaction kinetics.
1. "AEROSPACE APPLICATIONS OF SODIUM BATTERIES USING NOVEL CATHODE MATERIALS",

2. "ORGANIC CATHODE MATERIALS IN SODIUM BATTERIES"

3. "ADVANCED RECHARGEABLE SODIUM BATTERIES WITH NOVEL CATHODES"

4. "ELECTROCHEMISTRY OF METAL CHLORIDES IN SODIUM BATTERIES"

5. "ALTERNATE CATHODES FOR SODIUM - METAL CHLORIDE BATTERIES"

6. "SODIUM - METAL CHLORIDE BATTERY RESEARCH AT JPL"

7. "PROGRESS AND RECENT DEVELOPMENTS IN SODIUM - METAL CHLORIDE BATTERIES"
CONCLUSIONS

• RAPID DEVELOPMENT IN THE TECHNOLOGY OF Na / MCl₂ 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 / FeCl₂ AND Na / NiCl₂ CELLS.

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

• FUNDAMENTAL STUDIES CONFIRM THE CAPABILITIES OF THESE SYSTEMS.
  NiCl₂ EMERGES AS THE CANDIDATE CATHODE MATERIAL FOR HIGH POWER
  DENSITY APPLICATIONS SUCH AS ELECTRIC VEHICLE AND SPACE.