

## ADVANCES IN AMBIENT TEMPERATURE SECONDARY LITHIUM CELLS

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JPL is carrying out a NASA/OAST sponsored R & D program on the development of ambient temperature secondary lithium cells for future space applications. The goal of the program is to develop secondary lithium cells with a 100 Wh/kg specific energy and capable of 1000 cycles at 50% DOD. The approach towards meeting these goals initially focused on several basic issues related to the cell chemistry, selection of cathode materials and electrolytes and component development. We have examined the performance potential of Li-TiS<sub>2</sub>, Li-MoS<sub>3</sub>, Li-V<sub>6</sub>O<sub>13</sub> and Li-NbSe<sub>3</sub> electrochemical systems. Among these four, the Li-TiS<sub>2</sub> system was found to be the most promising system in terms of achievable specific energy and cycle life. Major advancements to date in the development of Li-TiS<sub>2</sub> cells are in the areas of cathode processing technology, mixed solvent electrolytes, and cell assembly. This paper summarizes these advances made at JPL on the development of secondary lithium cells.

## INTRODUCTION

Ambient temperature secondary lithium batteries have several intrinsic and potential advantages including higher energy density, longer active shelf life, and lower self discharge over conventional Ni-Cd, Ni-H<sub>2</sub>, Pb-acid and Ag-Zn batteries. Successful development of these batteries will yield large pay-offs such as 2-3 fold increase in energy storage capability and a longer active shelf life of 2 to 4 years over these systems. A detailed analysis of the strengths and weakness of secondary lithium batteries has indicated that these batteries are suitable for applications requiring less than 1 kW power and limited cycle life. Some of the projected space applications of these batteries are for Mars Rover, planetary space craft/probes, astronaut equipment, and geosynchronous spacecraft.

Several ambient temperature secondary lithium systems such as: Li-TiS<sub>2</sub>, Li-MoS<sub>2</sub>, Li-NbSe<sub>3</sub>, Li-MnO<sub>2</sub>, Li-V<sub>2</sub>O<sub>5</sub> etc. are currently under development for consumer and defense applications (1). Most of these systems are still in the research stage while a few of them are commercially available in small capacities (less than 1 Ah). Performance of the cells that are commercially available fall short

of meeting the space application requirements (2).

Under a NASA OAST sponsored program, Jet Propulsion Laboratory is developing ambient temperature secondary lithium cells for future space applications. The primary objective of the program is to develop ambient temperature secondary lithium cells with 100 Wh/kg specific energy while delivering 1000 cycles at moderate depths of discharge (50%). The major thrusts of this program are to improve cycle life and safety of these cells. Approach has involved work in three areas: 1) chemistry and material research, 2) component development and interactions, and 3) performance and safety. This paper describes the advances made at JPL to date in these areas.

## CHEMISTRY AND MATERIAL RESEARCH

Attempts to improve the performance capability of the state of art secondary lithium cells has been inhibited by the unavailability of materials with the desired properties and poor understanding of the cell chemistry(3). For these reasons the major emphasis of this effort has been directed towards identifying candidate electrode materials and a stable electrolyte and developing fundamental understanding of materials and cell chemistry. Some of the specific objectives in this area are : 1) Selection of a cathode material with a theoretical specific energy greater than 400 Wh/kg providing more than 1000 cycles, 2) Identification of an electrolyte that is stable towards lithium and has a conductivity greater than  $10^{-3} \text{ ohm}^{-1}\text{-cm}^{-1}$ , 3) Evaluation of the use of lithium alloys and other materials with low equivalent weight (40 gm/eq) to extend the cycle life performance and safety of the cells and 4) Development of concepts for overcharge/overdischarge protection of cells. Significant progress was made by JPL in the first three above topics as described below.

### Cathode Materials

Cathode materials required for these cells must possess several desirable properties such as high specific energy, good electrochemical rechargeability, good electronic conductivity, high lithium diffusivity, and chemical compatibility towards electrolyte. Several materials have been reported in the literature for use in secondary lithium batteries (3). These materials can be classified into two categories: transition metal chalcogenides ( $\text{TiS}_2$ ,  $\text{MoS}_3$ ,  $\text{MoS}_2$ ,  $\text{NbSe}_3$ , etc.) and transition metal oxides ( $\text{V}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{MnO}_2$ ,  $\text{CoO}_2$ , etc.). Lithium is inserted into these host structures electrochemically during discharge (Figure 1). Ideally, the host lattice may undergo only a minor structural change during lithium intercalation/insertion process (discharge), and return to its original state after charging process (the deintercalation). Four of these materials ( $\text{TiS}_2$ ,  $\text{MoS}_3$ ,  $\text{V}_6\text{O}_{13}$ , and  $\text{NbSe}_3$ ) were selected for detailed examination. These four materials were evaluated for their performance (specific energy, and cycle life) in experimental cells. In order to overcome poor

cycle life performance of the lithium electrode, a high lithium to positive electrode ("cathode") ratio (6:1) was used in these experimental cells. Major emphasis of this study was focussed on determining the cycle life capabilities of these cathode materials. The results of these studies are summarized in Table I. The results clearly indicate that the most promising cathode material is  $\text{TiS}_2$  in view of its long cycle life performance capability and realizable specific energy. The second material of choice is  $\text{NbSe}_3$ . Even though  $\text{MoS}_3$  and  $\text{V}_6\text{O}_{13}$  have higher theoretical specific energy, the materials showed poor cycle life performance and low useful specific energy. These studies led to the selection of  $\text{TiS}_2$  as the candidate cathode material for further studies with electrolytes and anode materials.

## Electrolytes

The ideal electrolyte required for ambient temperature secondary lithium cells must exhibit high conductivity, wide electrochemical operating window, high stability towards lithium, and compatibility with cathode materials and separator, low density, and low viscosity. Some of the electrolytes that have been investigated for this application are THF, 2-MeTHF, Methyl Formate, and Propylene Carbonate (4). These single solvent electrolytes provide only limited cycle life capability because of their reactivity towards lithium. It has been suggested (5) that the use of mixed solvent electrolytes may alleviate this problem due to the formation of a beneficial passivating film on the lithium anode and the synergistic effects associated with the use of the selected mixed solvents. A number of mixed solvent electrolytes are currently being investigated in our laboratory for use in Li- $\text{TiS}_2$  cells. These electrolytes contain 2-MeTHF and THF as the base solvents and Ethylene Carbonate (EC), Propylene Carbonate (PC) and 3-Methylsulfolane (3-MeS) as the co-solvents. The important properties such as conductivity, stability towards lithium and lithium cycling efficiency of these mixed solvent electrolytes were evaluated. Conductivity of the electrolytes was determined by standard methods. Stability of the electrolytes towards lithium was investigated by microcalorimetry. The heat evolved from the uncycled experimental cells in open circuit condition was measured at 25°C with a heat conduction Hart Scientific microcalorimeter. The cycling efficiency of lithium in various electrolytes was determined by cycling experimental Li- $\text{TiS}_2$  cells. The lithium cycling efficiency/ figure of merit (FOM) was calculated using the relationship:

$$\text{F.O.M.}_{\text{Li}} = \frac{\text{total accumulated discharge capacity}}{\text{theoretical Li capacity}}$$

Comparative performance of selected electrolytes is summarized in Table II. Among the co-solvents investigated, EC appears to be a

promising co-solvent. The mixed solvent electrolytes containing EC (EC/THF, EC/2-MeTHF, EC/THF/2-MeTHF, EC/3-MeS/2-MeTHF) showed higher conductivity and improved stability towards lithium compared to the electrolytes containing no EC (based on open circuit stand tests and microcalorimetry). The AC impedance and FTIR studies (6) indicated that the improved performance of EC/2-MeTHF electrolyte may be due to the formation of a thin  $\text{LiCO}_3$  film on the surface of the lithium electrode. From the results it can also be observed that EC containing electrolytes yielded higher FOM values than other electrolytes. A FOM of 38.5 was obtained with 10%EC+90%2-MeTHF electrolyte and this is 33% higher than the FOM of the bench mark 2-MeTHF electrolyte (29.5). Although the achievement of this FOM represents a significant advancement, the FOM value presently remains lower than the target objectives ( FOM ~ 80) . Work is continuing to identify an electrolyte that can meet program targets.

### **Lithium Alloys**

The limited cycle life performance of ambient temperature lithium cells is primarily attributed to the reactivity of the lithium anode with organic electrolytes. One method for reducing the reactivity of the lithium anode towards the electrolyte is by the use of lithium alloys as anode materials. Further, the use of lithium alloy anodes may also improve the safety of the cells. Six lithium alloys were selected for preliminary experimental evaluation after a detailed review of the literature. These alloys are Li-Al, Li-Si, Li-Sn, Li-Zn, Li-Pb, Li-Cd. All these materials are basically lithium rich alloys. These materials were selected based on their electrochemical potential, equivalent weight, lithium diffusivity, reversibility and thermodynamic stability towards organic electrolytes. Some of the important properties of these alloys are summarized in Table III. Experimental evaluation of these alloys was initiated on these anodes and is in progress.

### **COMPONENT DEVELOPMENT AND INTERACTIONS**

Component characteristics and cell design also play a significant role on cell performance. For this reason, work is in progress on the fabrication of  $\text{TiS}_2$  cathodes and design analyses. Details of the progress made in these two areas are described below.

#### **$\text{TiS}_2$ Cathode Processing**

The rate capability and faradaic utilization of  $\text{TiS}_2$  cathode are dependent on the chemical composition of  $\text{TiS}_2$ , nature of the binder, additives/ conducting diluents, as well as thickness and porosity of the electrode.  $\text{TiS}_2$  processed by the vapor transfer method was found to show higher faradaic utilization compared to the  $\text{TiS}_2$  materials procured from commercial sources (Table IV). This improved performance was found to be associated with purity

and stoichiometry of the material. Hence, it was decided to use  $\text{TiS}_2$  prepared in house by the improved vapor transport method in our future studies.

During cycling the cathode undergoes a volume change due to the intercalation/deintercalation of Li into/from  $\text{TiS}_2$  crystal lattice. The electrode structure must be capable of accommodating these changes, otherwise it will disintegrate during cycling. Studies carried on various binder materials identified EPDM as the most suitable binder material for the construction of  $\text{TiS}_2$  cathodes (7). Three methods : brushing, rolling, and pressing methods were examined for the fabrication of  $\text{TiS}_2$  cathodes. The brushing method was found to be suitable for the fabrication of small electrodes in the glove box. The rolling and pressing methods offered several advantages including amenability to scale up, and uniform loading. Typical characteristics of the electrodes fabricated by various methods is given Table V. Work is in progress to understand the relationships between electrode properties and performance.

### Design Trade off Studies

Some of the important parameters to be considered in the design of secondary lithium cell are ratio of electrode capacities, operating current density, electrolyte composition and quantity, case and grid materials and cell size. A computer program was developed (8) to understand the influence of these parameters on specific energy and to optimize the cell design. The results of these studies indicated that a specific energy of 80-100 Wh/kg is achievable for high capacity cells ( >20 Ah ). The negative to positive electrode capacity ratio has minimal effect on specific energy of the cells. A high anode to cathode capacity is required to account for the degradation of Li electrode and to achieve maximum cycle life. Cells cannot operate at current densities higher than 2 mA/cm<sup>2</sup> because of the poor conductivity of the electrolyte. The cell case is the major contributor to cell weight ( Fig. 2 ). Among the active materials, Li contributes the least to the overall weight. The collector grids contribute more to the weight than does lithium alone. The use of titanium cases and aluminum grids will reduce cell weight considerably. Experimental work is in progress to determine the influence of some of the important parameters on the cycle life performance of the cells.

### CELL PERFORMANCE AND SAFETY

An assessment was made of the status of secondary lithium cells by experimental evaluation of Li-MoS<sub>2</sub>, Li-NbSe<sub>3</sub> and Li-TiS<sub>2</sub> cells. Li-MoS<sub>2</sub> and Li-NbSe<sub>3</sub> cells (AA) were procured from the industry. The Li-TiS<sub>2</sub> cells were fabricated in house with non-optimize and cell hardware. These cells were evaluated for their charge/discharge characteristics, rate capability and cycle life. Performance characteristics of these cells is summarized in Table VI. These

cells have a cycle life of 100-250 cycles at moderate discharge rates ( C/5 ). Li-NbSe<sub>3</sub> cells exhibited high specific energy and Li-MoS<sub>2</sub> cells showed long cycle life. The low specific energy and cycle life of 5 Ah cells may be due to the non-optimize cell design and cell hardware. Some of the important problems identified are formation of soft shorts during cycling at low discharge rates ( C/10 ) and inferior performance at low depth of discharge in Li-MoS<sub>2</sub> system. Evaluation of the safety of these cells is in progress.

## CONCLUSIONS

Li-TiS<sub>2</sub> system appears to be the most promising system, among the ambient temperature secondary lithium systems examined, in view of its higher realizable specific energy and cycle life. Use of mixed solvent electrolytes was found to improve the cycle life of this system. Among the various electrolytes examined, 1.5 M LiAsF<sub>6</sub>/ EC + 2-MeTHF mixed solvent electrolyte was found to be more stable towards lithium. Experimental cells activated with this electrolyte exhibited more than 300 cycles at 100% DOD. Design trade off studies of this system indicated that a practical specific energy of 80-100 Wh/kg is achievable in 20 Ah cells and higher. The technology of these cells is still far from meeting the requirements of planetary space missions. Significant progress is still needed, particularly with respect to cycle life, tolerance to over-charge and over-discharge, safety and cell size. Many of these key problems require significant scientific and technological innovations in the areas of electrolyte technology, alternative lithium based anode materials, new additives and cell design.

## ACKNOWLEDGEMENTS

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## REFERENCES

- 1) B. B. Owens, "Survey of Lithium Ambient Temperature Secondary Systems", Fifth International Seminar on Lithium Battery Technology and Applications, Deerfield Beach, Fla, March 1989.
- 2) S. Subbarao et al, "Ambient Temperature Secondary Lithium Batteries for Space Applications", Proceedings of the Fourth Annual Battery Conference on Applications and Advances, Long Beach, CA, January, 1989.
- 3) K. M. Abraham, "Status of Rechargeable Positive Electrodes for Ambient Temperature Rechargeable Batteries", J. Power Sources 7, 1(1981).
- 4) V. R. Koch "Advances in Organic Electrolytes for Rechargeable Lithium batteries", Fourth International Seminar on Lithium Battery Technology and Applications, Deerfield Beach, Fla, March 1988.
- 5) S. Tobishima, M. Arakawa, T. Hirai and J. Yamaki, Journal of Power Sources, 20, P. 293-297 (1987).
- 6) D. H. Shen, S. Subbarao, F. Deliagiannis, and G. Halpert, "Evaluation of Mixed Solvent Electrolytes for Ambient Temperature Secondary Lithium Cells", Proceedings of the 33rd International Power Sources Symposium, p.45, (1988).
- 7) S. P. S. Yen, D. H. Shen, and R. B. Somoano, Journal of Electrochemical Society, 130, P.5, May (1983).
- 8) D. H. Shen, S. Subbarao, S. P. S. Yen and R. B. Somoano, Journal of Power Sources, 18, P127-131 (1986).

TABLE I. PERFORMANCE COMPARISON OF  
SELECTED CATHODE MATERIALS

MATL	OP. VOLTAGE	SPECIFIC ENERGY THEO.	EXPTL.	CYCLE LIFE 100% DOD
$\text{TiS}_2$	2.1	473	401	>600
$\text{MoS}_3$	1.9	717	243	40-60
$\text{V}_6\text{O}_{13}$ (NS)	2.15	622	323	30-50
$\text{NbSe}_3$	1.8	412	351	>100



# TABLE II PROPERTIES OF SELECTED ELECTROLYTES

ELECTROLYTE	CONDUCTIVITY $10^{-3}$ (OHM-CM) <sup>-1</sup>	STABILITY TO LITHIUM (microwatts)	LITHIUM CYCLING EFFICIENCY (FOM)
THF	13.7	90	3
2-MeTHF	3.4	25	28
10%EC+90%THF	14.6	84	4
10%EC+90%2-MeTHF	6.2	16	38
20%PC+90%2-MeTHF	6.1	24	-
25%3-MeS+75%2-MeTHF	3.6	-	10
50%THF+50%2-MeTHF	8.9	-	20

\* HEATOUT PUT ON OCV (MICROCALORIMETRY STUDIES)

\*\* DISCHARGE/CHARGE CURRENT DENSITY = 2/1 mA/cm<sup>2</sup>

# TABLE III. PROPERTIES OF LITHIUM ALLOYS

ALLOY	EQ. WT (g/eq)	E vs Li (mV)	Ah/g	DIFFUSIVITY (cm <sup>2</sup> /sec)	SP. ENERGY* (Wh/kg)
Li	6.9	0	3.86	—	473
Li <sub>2.5</sub> Al	18.3	141	1.46	10 <sup>-4</sup> **	403
Li <sub>2</sub> Si	21.0	332	1.28	10 <sup>-5</sup> **	356
Li <sub>4.5</sub> Pb	68.1	400	0.39	10 <sup>-8</sup> ***	253
Li <sub>5.6</sub> Sn	34.2	263	0.78	10 <sup>-5</sup> **	337
Li <sub>1.5</sub> Zn	68.9	106	0.39	10 <sup>-9</sup> ***	295

\* CALCULATED FOR LI-TIS<sub>2</sub> SYSTEM

\*\* 400° C

\*\*\* 25° C

TABLE IV. PROPERTIES OF  $\text{TiS}_2$  RAW MATERIAL

SOURCE	STIOCHOMETRY (S : Ti)	IMPURITIES	AP. DENSITY (g/cc)	FARADAIC UTILIZATION (% THEO.)
JPL	1.99	O	0.80	95
DEGUSSA	1.97	Cl	0.48	75
CERAC	2.18	Cl,S	0.32	60

# TABLE V. PROPERTIES OF $\text{TiS}_2$ CATHODES

PROPERTY	BRUSHING	ROLLING	PRESSING
THICKNESS (mil)	15+2	20+2	16+2
LOADING (mg/cm <sup>2</sup> )	48+5	66+5	54+5
POROSITY (%)	56+2	56+2	54+2
CAPACITY (mAh/cm <sup>2</sup> )	12+1	16+1	13+1

FIG. 1. STRUCTURE AND INTERCALATION OF  
Li IN  $\text{TiS}_2$

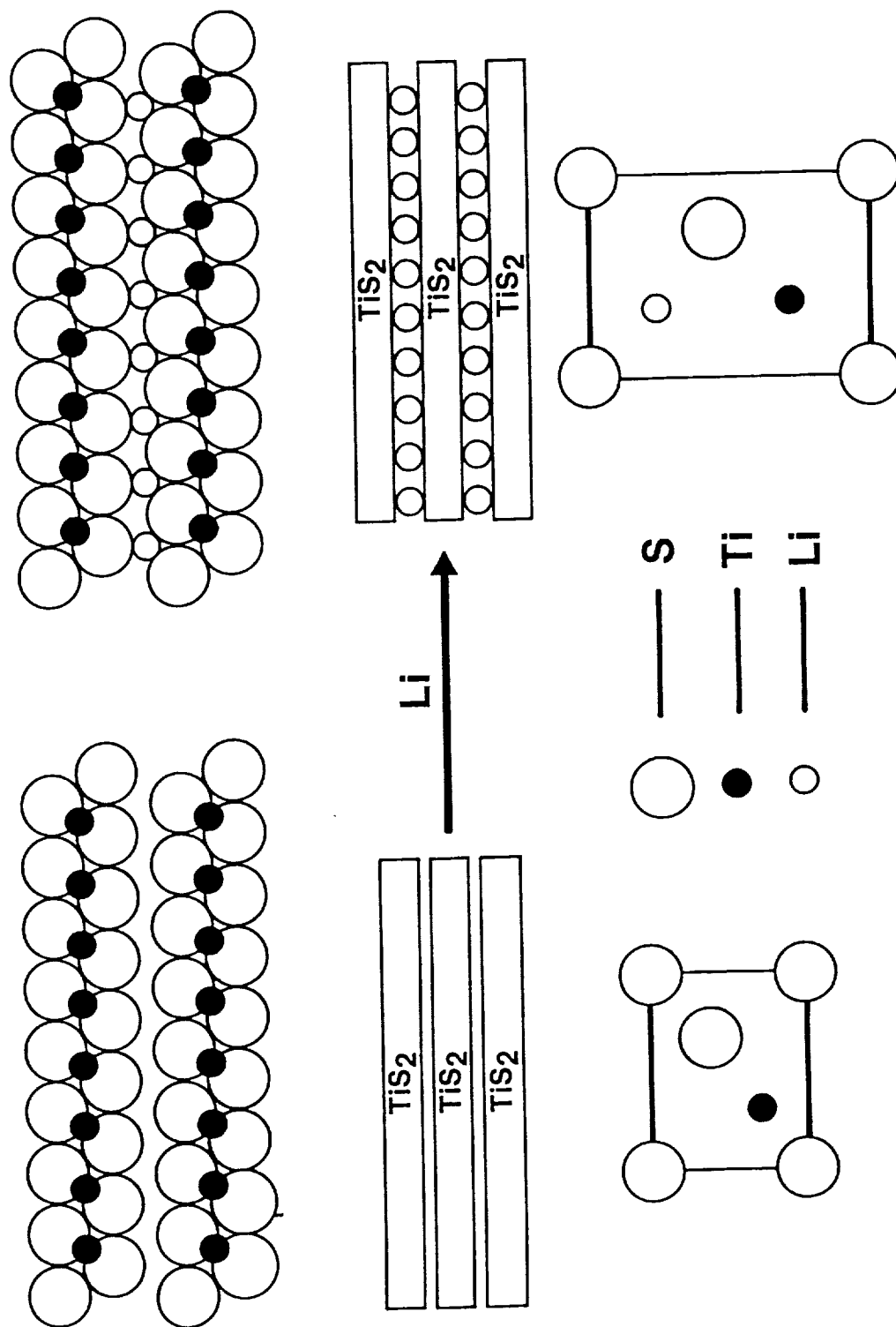
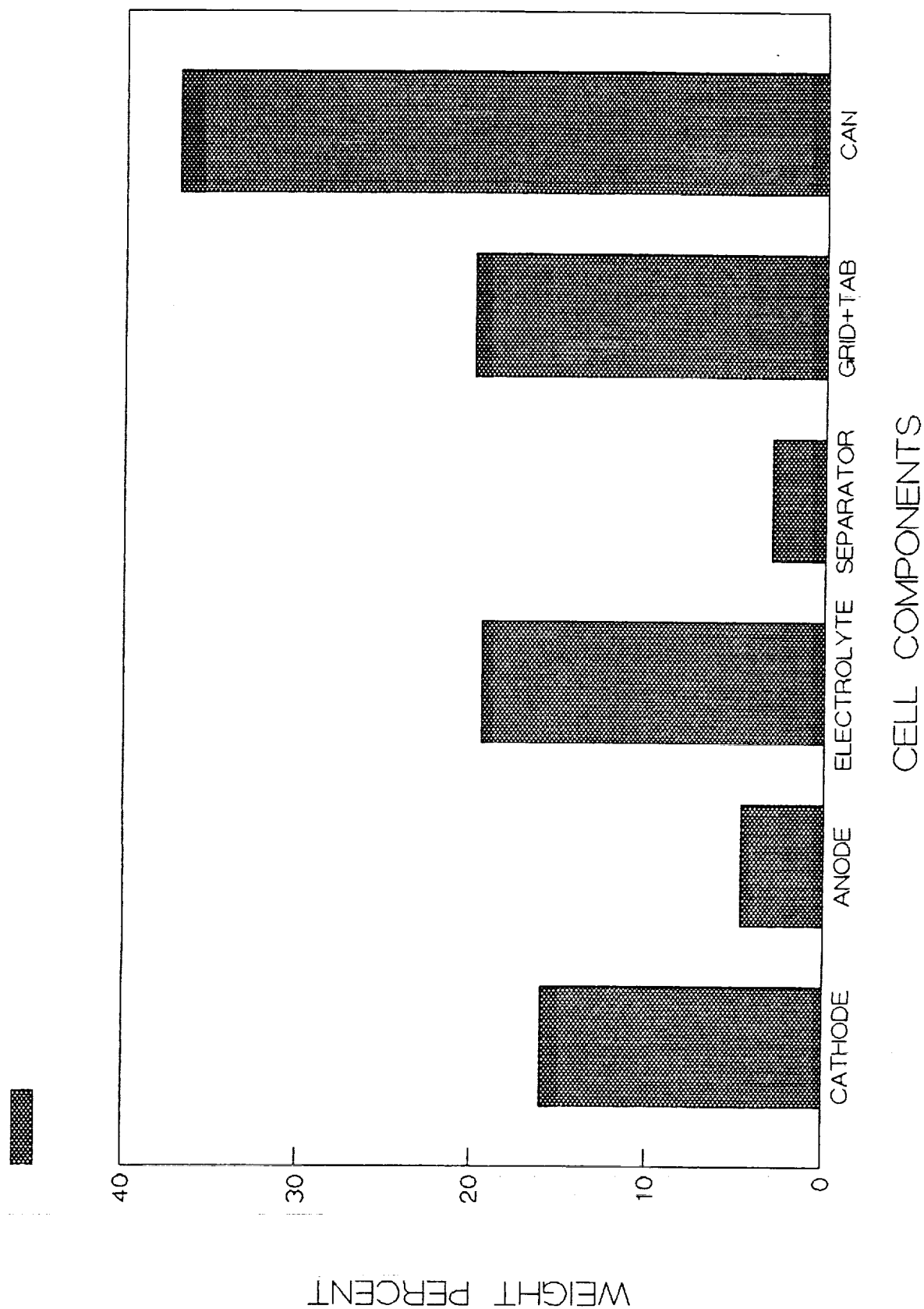


FIG.2. 5 Ah Li-TiS<sub>2</sub> CELL WEIGHT BUDGET





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**ADVANCED CONCEPTS**

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**SUMMARY**

**ADVANCED CONCEPTS**

- COLD FUSION

**LAST YEAR'S ADVANCED CONCEPTS**

- HIGH TEMPERATURE BATTERIES:
  - COMPOSITE SOLID ELECTROLYTES
  - BIPOLAR Li Al - Fe S<sub>2</sub>, Li Al - S, (?) Li - O<sub>2</sub>
  - NEW MATERIALS
- HIGH TEMPERATURE FUEL CELLS
  - MONOLITHIC AND PSEUDOMONOLITHIC
  - NEW ELECTROLYTES
- LOW TEMPERATURE SYSTEMS
  - ULTRACAPACITORS
  - NEW Li SYSTEMS
  - NEW COUPLES AND DESIGNS

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### APPLICATIONS WILL DETERMINE WHICH ADVANCED SYSTEM IS BEST

- FOR LEO, REQUIREMENTS ARE
  - HIGH ENERGY DENSITY
  - HIGH CYCLE LIFE (>30,000 CYCLES)
  - HIGH POWER DENSITY

POSSIBLE CANDIDATES: SOLID ELECTROLYTE SYSTEMS; RFC's
- FOR PLANETARY ROVER, REQUIREMENTS ARE
  - HIGH ENERGY DENSITY
  - VERY HIGH POWER DENSITY
  - 1000 CYCLES

POSSIBLE CANDIDATES:  $\text{LiAl-FeS}_2$ , FUEL CELL, Na/BETA/METAL CHLORIDES
- FOR SPACE PROBES, MANPACK, SMALL GEO SPACECRAFTS
  - HIGH ENERGY DENSITY
  - SMALL SIZE
  - 1000 CYCLES
  - LOW TEMPERATURE OPERATION (5-20°C)

POSSIBLE CANDIDATES: AMBIENT TEMP. LITHIUM; POLYMER ELECTROLYTE SYSTEMS
- FOR MOON BASE OR MARS OUTPOST, REQUIREMENTS ARE
  - EXTREMELY HIGH ENERGY DENSITY
  - EXTREMELY HIGH RELIABILITY

POSSIBLE SYSTEMS: NUCLEAR; RFC

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### COLD FUSION

- IF TRUE, WILL RADICALLY CHANGE THINKING
- BASELOAD FOR LUNAR BASE
- POSSIBLY PROPULSION: SPECIFIC POWER IS KEY; ESPECIALLY IF NO SHIELDING REQUIRED
- MUST GIVE HIGH-QUALITY HEAT (300°C FOR RANKINE, PREFERABLY 1000°C, BRAYTON, OTHERS)
- IMPLEMENTATION OF 1000°C, MOLTEN  $^6\text{LiD}$ ?
- SMALL SYSTEMS: STIRLING, Na HEAT ENGINE, POSSIBLY THERMIONICS, THERMOELECTRICS
- CLASSICAL CYCLES SINCE NO  $\gamma$ - OR  $n$ - TO ELECTRICITY DEVICES EXIST
- QUESTIONS: STANDBY POWER CAPABILITY?

LOAD-LEVELING BATTERIES OR REGENERATIVE FUEL CELLS WILL BE  
NECESSARY, OR OFF-PEAK POWER CAN BE USED FOR PROPELLANT  
MANUFACTURE

- WHILE EXCITING, IF TRUE, WILL TAKE A LONG TIME TO IMPLEMENT. SO WE NEED TODAY'S  
SYSTEMS AND LAST YEAR'S NEW CONCEPTS. RISK LEVEL - VERY HIGH: REQUIRES A CONFIRMATION  
IF APPLICABLE, SYSTEMS & MATERIALS DEVELOPMENT

TIME FRAME: 2015.†

EFFORT: AS FISSION

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### HIGH TEMPERATURE BATTERIES

- COMPOSITE SOLID ELECTROLYTES
  - IMPROVEMENTS IN NaS AND OTHER SYSTEMS (Na/TRANSITION METAL CHLORIDES, Li SYSTEMS)
  - REQUIRE NEW GEOMETRIES, BETTER PACKAGING
  - LOWER TEMPERATURES OF CHLORIDE SYSTEMS MAY GIVE BETTER LIFE
  - SHOULD BE VERY SAFE (INSOLUBLE CHLORIDES IN  $\text{NaAlCl}_4$ ;  $\text{NaFeCl}_4$  UNSAFE)
- $\text{LiAl-FeS}_2$  BIPOLAR: 210 Wh/kg  
REQUIRE Mo-PLATED BIPOLAR COLLECTOR, SEALS
- $\text{Li/O}_2$  (?)
- $\text{LiAl-S}$ , SOLID ELECTROLYTE: 300 Wh/kg
- NEW HIGH-TEMPERATURE MATERIALS, e.g., COATED CARBON-CARBON (INSULATING OR CONDUCTING, HIGHLY CORROSION RESISTANT)

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### HIGH TEMPERATURE FUEL CELLS

- MONOLITHIC AND PSEUDOMONOLITHIC STRUCTURES (EXTRUSION, ETC)
- MONOLITHIC ELECTROLYZERS (MAY USE WITH LOW-TEMPERATURE FUEL CELL)
- LOW-TEMPERATURE SOLID ELECTROLYTES FOR FUEL CELLS

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### LOW-TEMPERATURE SYSTEMS

- 20,000 J, 5 Wh/kg ULTRACAPACITORS
  - HIGHER VOLTAGE REQUIRED (ORGANICS, LOW TEMPERATURE MOLTEN SALTS)
  - HIGHER FARADAIC PSEUDOCAPACITANCE ( $250 \mu\text{F}/\text{cm}^2$ )
  - HIGHER AREAS
- LI POLYMER ELECTROLYTES
  - NEW STRUCTURES (OTHER THAN  $\text{PEO}/\text{CF}_3\text{SO}_3^-$ )
  - AUTONOMOUS LI CONDUCTORS
- LI - METAL OXIDE CATHODES ( $\text{CoO}_2$ ,  $\text{MnO}_2$ )
  - PROBLEM OF CHARGE POTENTIAL WINDOW
- NEW AQUEOUS COUPLES ( $\text{H}_2$ -BI/ $\text{MnO}_2$ , etc)
- NEW DESIGNS WITH OLD COUPLES (BIPOLAR, e.g., WITH  $\text{Ni}/\text{H}_2$ )
- RELIABLE, TRUE "SINGLE-CAN" REGENERATIVE FC/ELECTROLYZER

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### GENERAL COMMENTS

- RELIABILITY vs WEIGHT & COST TRADE-OFF FOR SPACECRAFT
  - HIGH CAPABILITY (LOW WEIGHT, VOLUME, ETC.) MUST BE CONSISTENT WITH RELIABILITY
- MOST FUNDS ARE SPENT ON EXISTING SYSTEMS. NEW SYSTEMS NEED A RELIABILITY ANALYSIS BEFORE FUNDS ARE COMMITTED FOR PILOT PRODUCTION OF INAPPROPRIATE DESIGNS FOR MISSION
- ACCELERATED TESTING REQUIRED: WEIBULL AND OTHER ANALYSIS
- RISK LEVEL
  - IS THERE A WAY OUT IF THE APPROACH DOES NOT WORK? ARE THERE ALTERNATIVE OPTIONS?
  - OPTIONS AVOID RISK
- TIME FRAME, LEVEL OF EFFORT
  - VARIABLE FROM TRANSFER TO PRIVATE SECTOR; SMALL EFFORT TO (FOR FUSION, IF TRUE) MASSIVE PROGRAM

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**HYDROGEN-OXYGEN FUEL CELLS AND ELECTROLYZERS**

**FUTURE MISSIONS BENEFITED**

- NEAR-EARTH
- PATHFINDER
- UNSPECIFIED - AS YET UNDEFINED

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### NEAR-EARTH MISSIONS

- INTEGRATED FUEL CELL - ELECTROLYZER

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### PATHFINDER

- LONG-LIFE, RELIABLE, EFFICIENT PEM AND ALKALINE FUEL CELLS  
AND ELECTROLYZERS

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**UNDEFINED MISSIONS**

- LONG-LIFE, RELIABLE, EFFICIENT, COMPACT PRIMARY OR REGENERATIVE FUEL CELL SYSTEMS

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**THESE SYSTEMS ARE ENABLING FOR THE INDICATED MISSIONS**

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### TECHNOLOGY ISSUES

- COMPONENT LIFE TESTS IN FULL PLANAR AREA HARDWARE

- FAILURE MECHANISMS
- REACTANT CROSSOVER
- CORROSION
- DEVELOPMENT OF PREDICTIVE MODELS

JH89 SERT 06



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### DEVELOPMENTAL NEED

- PASSIVE SYSTEM OPERATION FOR HIGH RELIABILITY

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**RESEARCH ISSUES**

NO PROVISION FOR LONG-TERM RESEARCH IN MISSION DRIVEN PROGRAMS

JH89 SERT 08



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**NICKEL ELECTRODE WORKSHOP**

CHAIRPERSON: ALBERT ZIMMERMAN

CO-CHAIRPERSON: MARGARET REID

APRIL 12, 1989

MR89 SERT 01



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### ADVANCED NICKEL ELECTRODE TECHNOLOGY

- LIGHTWEIGHT NICKEL ELECTRODES (OPTIMIZED FOR HIGH ENERGY DENSITY)
  - SINTERED
  - FIBER
- NICKEL ELECTRODES OPTIMIZED FOR LONG CYCLE LIFE
  - OPTIMIZED SUPPORTING POROUS STRUCTURES
- TECHNOLOGY MAINTENANCE

MR89-SERT.02



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### APPLICATIONS

- LIGHTWEIGHT NI ELECTRODES
  - MODERATE CYCLE LIFE (~ 1000 CYCLES, > 50% DOD)
  - HIGH ENERGY DENSITY (~ 100 Wh/kg)
  - MARS ROVER
- LONG-LIFE NI ELECTRODES
  - > 30,000 CYCLES (50% DOD)
  - SPACE STATION
  - 10-20 YR (GLOBAL CHANGE TECHNOLOGY MISSIONS)
- TECHNOLOGY MAINTENANCE
  - ASSURE HIGH RELIABILITY FOR EVOLVING TECHNOLOGY

MR89-SERT.03





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### CRITICAL TECHNOLOGY NEEDS

- **STRUCTURAL INSTABILITY**
  - SWELLING
  - EXTRUSION
  - LOSS OF OHMIC CONTACT WITH CURRENT COLLECTOR
- **IMPROVED ACTIVE MATERIAL MECHANICAL PROPERTIES**
  - ADDITIVES
  - ELECTROLYTE
- **IMPROVED TEST PROCEDURES (TECHNOLOGY SUPPORT)**
  - ACCELERATED/REAL TIME
  - LOT CONFIRMATION TESTING
  - ROUTINE DPA OF CELL ON LOT BASIS
- **MODELING**
  - INPUTS - IMPEDANCE, PORE DISTRIBUTIONS, ETC.
  - ANALYTICAL METHODS
    - CORRELATION OF ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS

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### RESEARCH NEEDS

- **CAUSES FOR STRUCTURAL INSTABILITY**
  - ACTIVE MATERIAL MOVEMENT/SHEDDING
  - SINTER FRACTURING
  - SHORTING: DETECTION AND CAUSES
- **CORROSION RATES**
  - INHIBITION
  - ACCELERATING FACTORS
- **ADDITIVES**
  - IMPROVED CHARGE EFFICIENCY
  - IMPROVED CAPACITY (INCREASED UTILIZATION OF NI)
- **ELECTROLYTE CONCENTRATION - EFFECTS ON PERFORMANCE**
- **INTERACTIONS WITH HYDROGEN GAS**
  - STORAGE
  - SELF-DISCHARGE
  - EFFECT ON CAPACITY, SECOND PLATEAU EFFECTS

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### RESEARCH NEEDS

- TESTING
  - CHARGE CONTROL METHODS
- SCALE-UP
  - EVALUATE PRESENT ASSUMPTIONS OF LINEAR SCALING
  - EXAMINE LIFE TEST DATA AND FAILURE MODES
- FUNDAMENTAL ELECTROCHEMISTRY OF NI ELECTRODE PROCESSES
  - APPLICATION OF NOVEL ANALYTICAL TECHNIQUES  
(CALORIMETRY, NEUTRON SCATTERING, ACOUSTIC EMISSION,  
NOISE SPECTRUM ANALYSIS, EXAFS)

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## SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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### SUMMARY

- CELLS CONTAINING NI ELECTRODES ARE ONLY ESTABLISHED  
LONG CYCLE LIFE TECHNOLOGY
  - RELIABLE
  - SAFE
- IMPROVEMENTS SHOULD BE SUPPORTED AND ARE ACHIEVABLE
  - OPTIMIZATION FOR HIGH ENERGY DENSITY
  - OPTIMIZATION FOR LONG CYCLE LIFE
- TECHNOLOGY MAINTENANCE PROGRAM SHOULD BE INSTITUTED
  - ASSURE CONTINUED RELIABILITY
  - SMOOTHLY TRANSITION ADVANCED TECHNOLOGY INTO PRACTICE

MR89 SERT 07



# SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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APRIL 11-13, 1989

## WORKSHOP ON ADVANCED RECHARGEABLE BATTERIES

G. HALPERT AND J. SMITHRICK

## SPACE ELECTROCHEMICAL R&T CONFERENCE

APRIL 12, 1989

GH/JS89-SERT 01



# SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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PRIORITY	CHARGE/ DISCHARGE DURATIONS	APPLICATIONS TYPICAL OPERATIONAL CYCLES REQUIRED			TYPICAL PEAK POWER AND ENERGY STORAGE REQUIRED (5 MINUTES)
		ACTUAL	QUAL*	DESIRED	
1 OUTER PLANETARY ORBIT	C - 2 hr D - 0.7 hr	500	1,000	2,000	0.5 C (1 kWh)
2 INNER PLANETARY ORBIT	C - 2 hr D - 0.7 hr	3,000	6,000	10,000	1.5 C (2 kWh)
3 GEO	C - 22.8 hr D - 1.2 hr	1,500	2,000	4,000	1.5 C (5 kWh)
4 PLANETARY ROVER	C - 12 hr D - 3 hr	300	600	800	1.3 C (3 kWh)
5 LUNAR BASE	C - 11 DAYS D - 17 DAYS	80	160	350	0.02 C (5 MWh)
6 LEO	C - 1 hr D - 0.6 hr	30,000	35,000	50,000	1.1 C (25 kWh)

GEO = GEOSYNCHRONOUS ORBIT

LEO = LOW EARTH ORBIT

\*QUAL = MINIMUM NUMBER OF CYCLES NEEDED TO QUALIFY FOR APPLICATION

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### OTHER NASA APPLICATIONS

- FREE FLYERS
- ROBOTICS
- OMV
- ASTRONAUT EQUIPMENT
- PENETRATORS/PROBES
- TETHERED S/C

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### ASSUMPTIONS

- NO COST CONSTRAINTS
- TECHNOLOGY DEMONSTRATION - LEVEL 5 ASSUMES LIMITED TESTING TO VERIFY CAPABILITY
- BIPOLAR TECHNOLOGY - NOT A LIMITATION
- SPECIFIC ENERGIES BASED ON BATTERY CAPACITY

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# SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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## CANDIDATES FOR LARGE POWER SYSTEMS (>2.5 kWh)

"BEST CASE ANALYSIS"

SYSTEM	PROJECTED SPECIFIC ENERGY (Wh/kg)	APPLICATIONS	YEAR FOR PROJECTED TECHNOLOGY DEMO (LEVEL 5)
Na - S	150	4,5	2000
Na - S	150	3,6	2010
Na - S	200	4,5	2010
Na - S	200	3,6	2015
Li (Al) - FeS <sub>2</sub>	175	4,5	2000
Li (Al) - FeS <sub>2</sub>	175	3	2010
Na - MCl <sub>x</sub>	160	4,5	2000
Na - MCl <sub>x</sub>	160	3,6	2010
Adv Ni-H <sub>2</sub>	70	3,4,5	1995
Adv Ni-H <sub>2</sub>	70	6	2000

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# SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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## CANDIDATES FOR SMALL POWER SYSTEMS (<2.5 kWh)

"BEST CASE ANALYSIS"

SYSTEM	PROJECTED SPECIFIC ENERGY (Wh/kg)	APPLICATIONS	YEAR FOR PROJECTED TECHNOLOGY DEMO (LEVEL 5)
LI - SOLID CATHODE (TiS <sub>2</sub> , NbSe <sub>3</sub> , V <sub>6</sub> O <sub>13</sub> )	100	1	1990
(SAME AS ABOVE)	100	3	1995
LI - SOLID CATHODE (CoO <sub>2</sub> )	200	1,3	2005
LI - P.E. - SOLID CATHODE	200	1,3	2005
(SAME AS ABOVE)	200	2	2010

\*P.E. = POLYMERIC ELECTROLYTE

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## SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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### TECHNOLOGY ISSUES

Na-S (200 Wh/kg)

- REDESIGN CELL/BATTERY (200 Wh/kg)
- CORROSION FOR LONG-LIFE APPLICATIONS (>2 YRS)
- ELECTROLYTE SEALING
- CONTROL OF FAILURE MODE
- FREEZE/THAW
- LARGE SYSTEMS (2.5-100 kWh)
- STATE-OF-THE-ART - 140 Wh/kg
- PROBABILITY OF SUCCESS - 80%

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### TECHNOLOGY ISSUES

U.P. LI-(Al)-FeS<sub>2</sub> (175 Wh/kg)

- CELL REDESIGN
- CORROSION FOR LONG-TERM APPLICATION
- HERMETIC SEAL FOR CELL
- ELECTROLYTE AND SEPARATOR MODIFICATION
- CELL EQUALIZATION
- STATE-OF-THE-ART - 140 Wh/kg
- PROBABILITY OF SUCCESS - 60%

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### TECHNOLOGY ISSUES

Na -  $\text{MCl}_x$  (160 Wh/kg)

- CELL REDESIGN
- CHEMISTRY CLARIFICATION
- TECHNOLOGY RESIDES OUTSIDE U.S.
- SEAL DEVELOPMENT
- TIME-DEPENDENT FAILURE MECHANISMS IDENTIFIED
- FREEZE/THAW IS REPORTED AS A NON-ISSUE
- PROBABILITY OF SUCCESS - 50%

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### TECHNOLOGY ISSUES

ADVANCED  $\text{Ni-H}_2$  (70 Wh/kg)

- MODIFY SUPPORT STRUCTURES FOR COMPONENT, CELL  
AND BATTERY
- TECHNOLOGY FLIGHT DEMO/QUALIFIED
- PROBABILITY OF SUCCESS - 95%

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## SPACE ELECTROCHEMICAL RESEARCH & TECHNOLOGY CONFERENCE

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### TECHNOLOGY ISSUES

LI - SOLID CATHODE (200 Wh/kg)

- LI RECHARGEABILITY
- ELECTROLYTE STABILITY AND CONDUCTIVITY
- HIGHER ENERGY LONG-LIFE CATHODES REQUIRED ( $\text{CoO}_2$ )
- SCALE-UP FROM CONSUMER SIZES
- SAFETY
- PROBABILITY OF SUCCESS - 60%

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### TECHNOLOGY ISSUES

LI - POLYMER ELECTROLYTE - SOLID CATHODE (200 Wh/kg)

- MANUFACTURING PROCESSING OF P.E.
- P.E. COMPOSITION AND CONDUCTIVITY
- INTERFACIAL CONTACT
- PROBABILITY OF SUCCESS - 60%

GHJS89-SERT 03