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Cathodes For Molten-Salt Batteries

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This presentation is related to research on cathodes for molten-salt rechargeable lithium batteries for pulse power applications. The support of this Phase I SBIR program by the US Army Labcom, ETDC is gratefully acknowledged.

CATHODES FOR MOLTEN SALT BATTERIES

- INTRODUCTION
- EXPERIMENTAL CELL
- RESULTS AND DISCUSSION
- PERFORMANCE PROJECTION
- CONCLUSIONS

For the cathode reactions in molten-salt cells, chlorine-based and sulfur-based cathodes reactants have relatively high exchange current densities. Sulfur-based cathodes, metal sulfides and disulfides have been extensively investigated. Primary thermal batteries of the Li-alloy/FeS_2 variety have been available for a number of years. In this research effort chlorine based rechargeable cathodes have been investigated for the pulse power application. A brief introduction is followed by the experimental aspects of research, and the results obtained. Performance projections to the battery system level are discussed and the presentation is summarized with conclusions.

INTRODUCTION

PHASE I SBIR PROGRAM OBJECTIVE

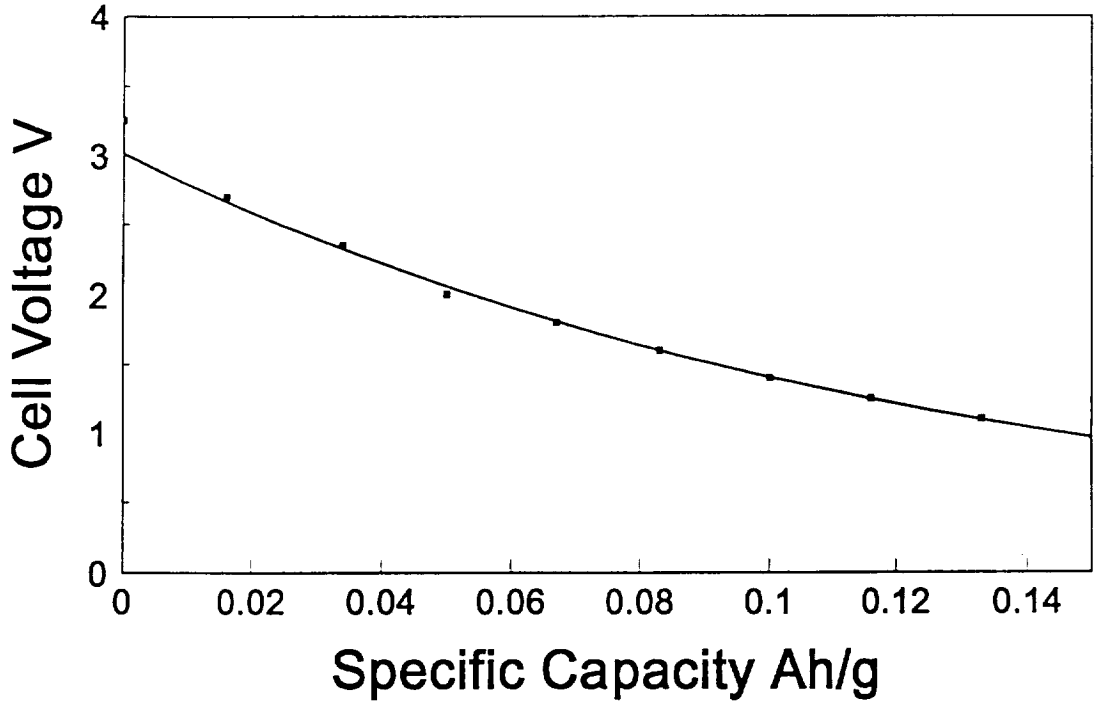
- RECHARGEABLE CHLORINE CATHODE ADDITIVES
- HIGH RATE CARBON CATHODES

In this battery system, during charge lithium is deposited to form the lithium aluminum alloy and chlorine formed is stored by adsorption on a high surface area carbon cathode. During discharge, lithium and chlorine dissolution reactions produce lithium chloride. Chlorine can be stored during charge as adsorbed chlorine or as a chlorine adduct. The objectives of this Phase I program are (1) to identify chlorine cathode additives to augment the storage capacity and (2) develop high rate carbon cathode structure while incorporating these additives.

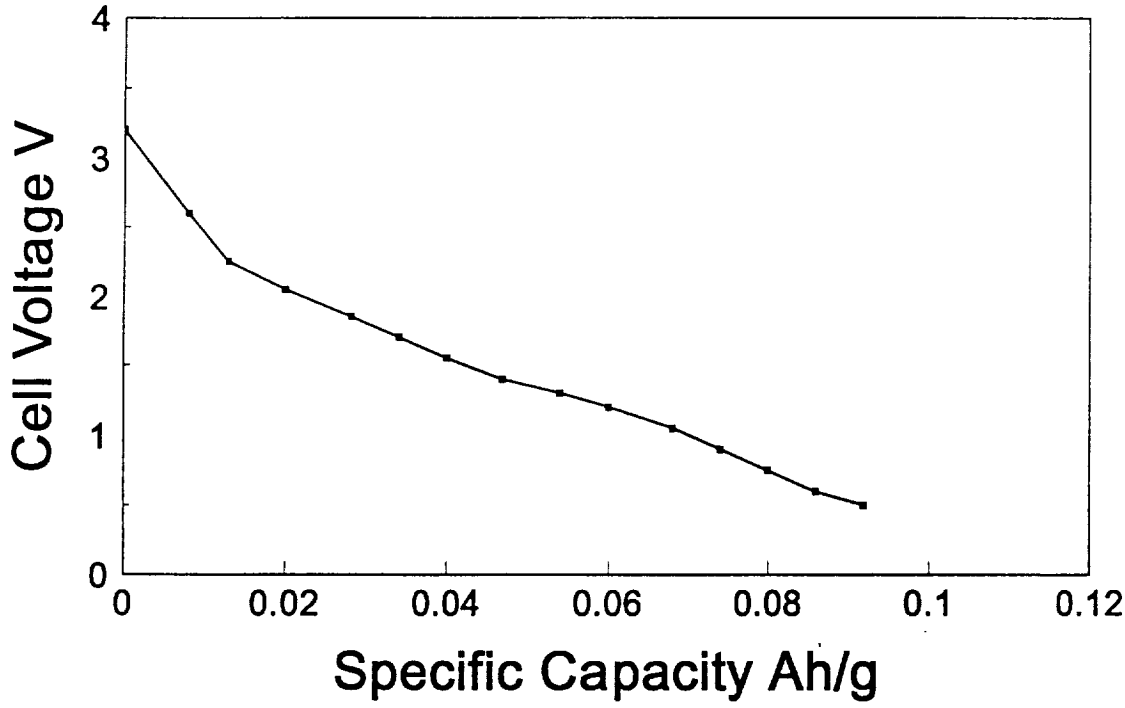
EXPERIMENTAL

- WAFER-STACK CELL
- NOMINAL 2" DIAMETER CELLS
- Li-Al ALLOY WAFERS
- CARBON BASED CATHODES
    - Tungsten carbide
    - Tungsten Disulfide
    - Molybdenum Disulfide
    - Vanadium Oxide
    - Tungsten Oxide
- LiCl-KCl SALT SEPARATOR WAFERS

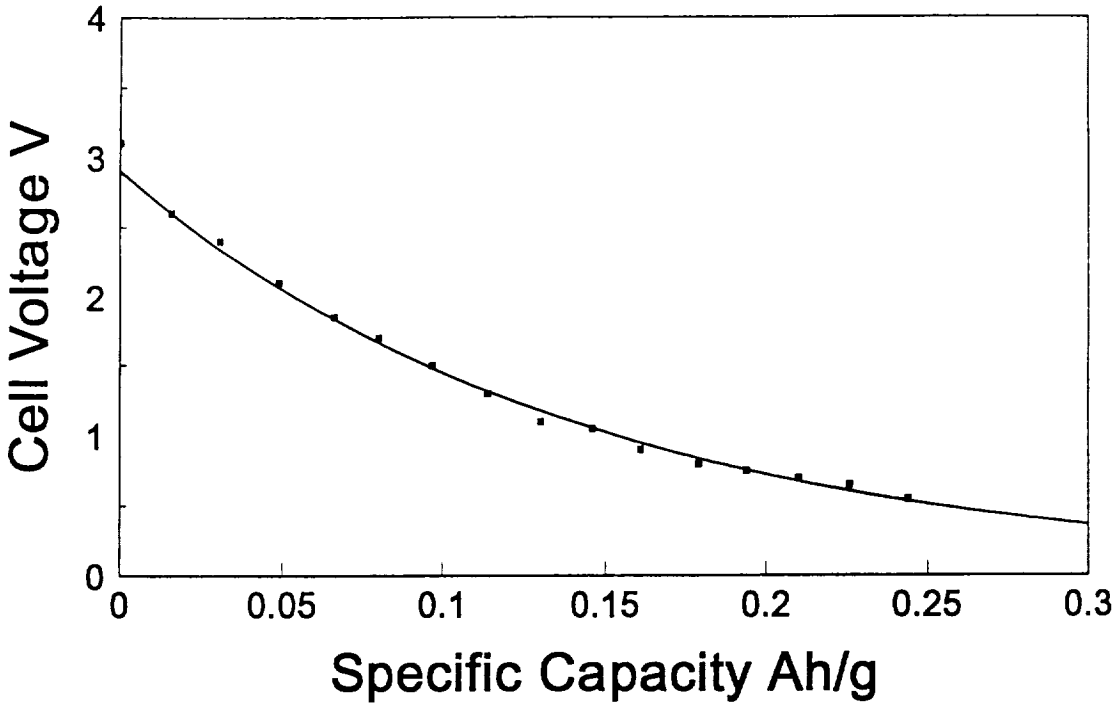
Experimental work was carried out with nominally 2" diameter wafer stack configuration cells, Li-Al anode wafer, LiCl-KCl salt separator wafer containing a molten-salt immobilizer compound and the carbon cathode wafer were used to form the cell. Additives identified above were incorporated in the carbon cathode wafers, using standard techniques.



Cell discharge profile for a Li-Al/carbon cathode cell, after being charged to a constant voltage of 3.30 V, is shown in this viewgraph. The cell voltage versus specific cathode capacity at 62 mA/cm^2 is shown for a plain carbon cathode. Please note the specific capacity is for cathode weight alone.



This viewgraph shows a similar discharge profile for a carbon cathode, incorporating tungsten carbide as the additive. The lower specific cathode capacity can be ascribed to the high specific gravity of tungsten carbide.



This discharge is for a cell consisting of a cathode that has tungsten disulfide as the additive. This cathode yields good capacity, while functioning as a chlorine cathode.

RESULTS

Discharge Capacities at Constant Current for Carbon + Additive Cathodes in Li-Al Molten Salt Cells

Cathode Type	OCV, V	Current Density, mA/cm^2	Sp. Cath. Cap. Ah/g
Carbon	3.30	62	0.18
VO_x + C	2.60	62	0.18
WO_3 + C	2.85	62	0.17

This table shows specific cathode capacity for three cathodes, carbon, VO_x + C, and WO_3 + C

RESULTS

Discharge Capacities at Constant Current for Carbon + Additive Cathodes in Li-Al Molten Salt Cells

Cathode Type	OCV, V	Current Density, mA/cm^2	Sp. Cath. Cap. Ah/g
WC + C	3.20	62 186	0.10 0.09
MoS_2 + C	2.80	62 124	0.14 0.14

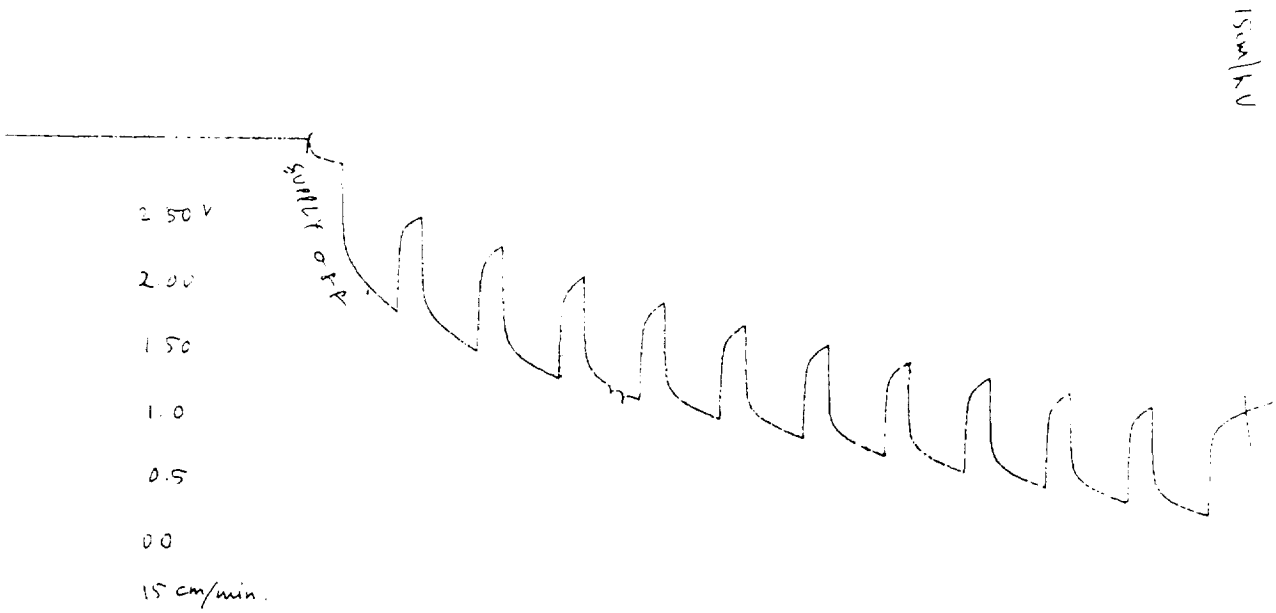
This viewgraph shows the specific cathode capacity for WC and MoS_2 as cathode additives.

RESULTS

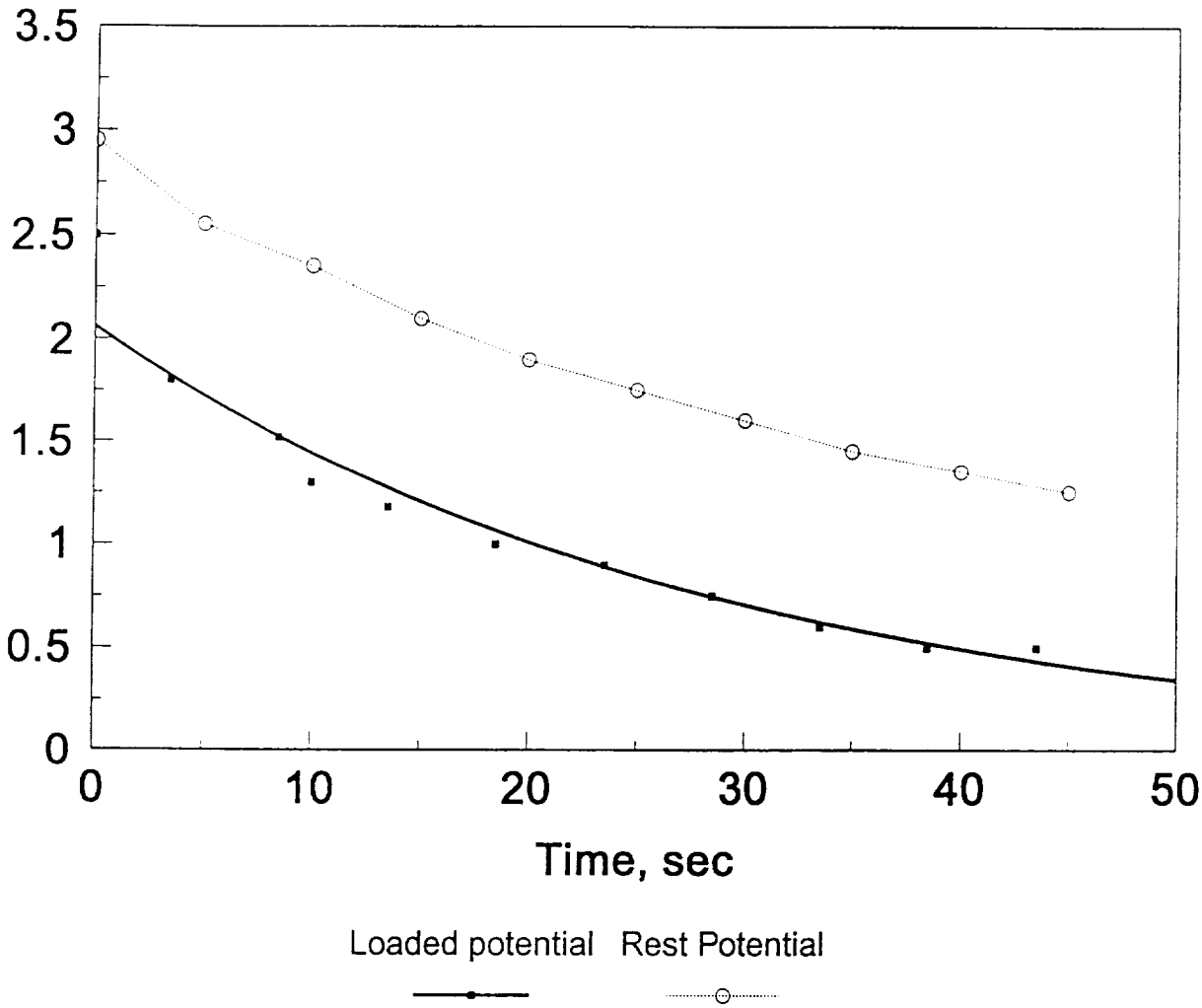
Discharge Capacities at Constant Current for Carbon + Additive Cathodes in Li-Al Molten Salt Cells

Cathode Type	OCV, V	Current Density, mA/cm^2	Sp. Cath. Cap. Ah/g
WS_2 + C	3.10	62	0.17
		124	0.21
		186	0.13
		248	0.17

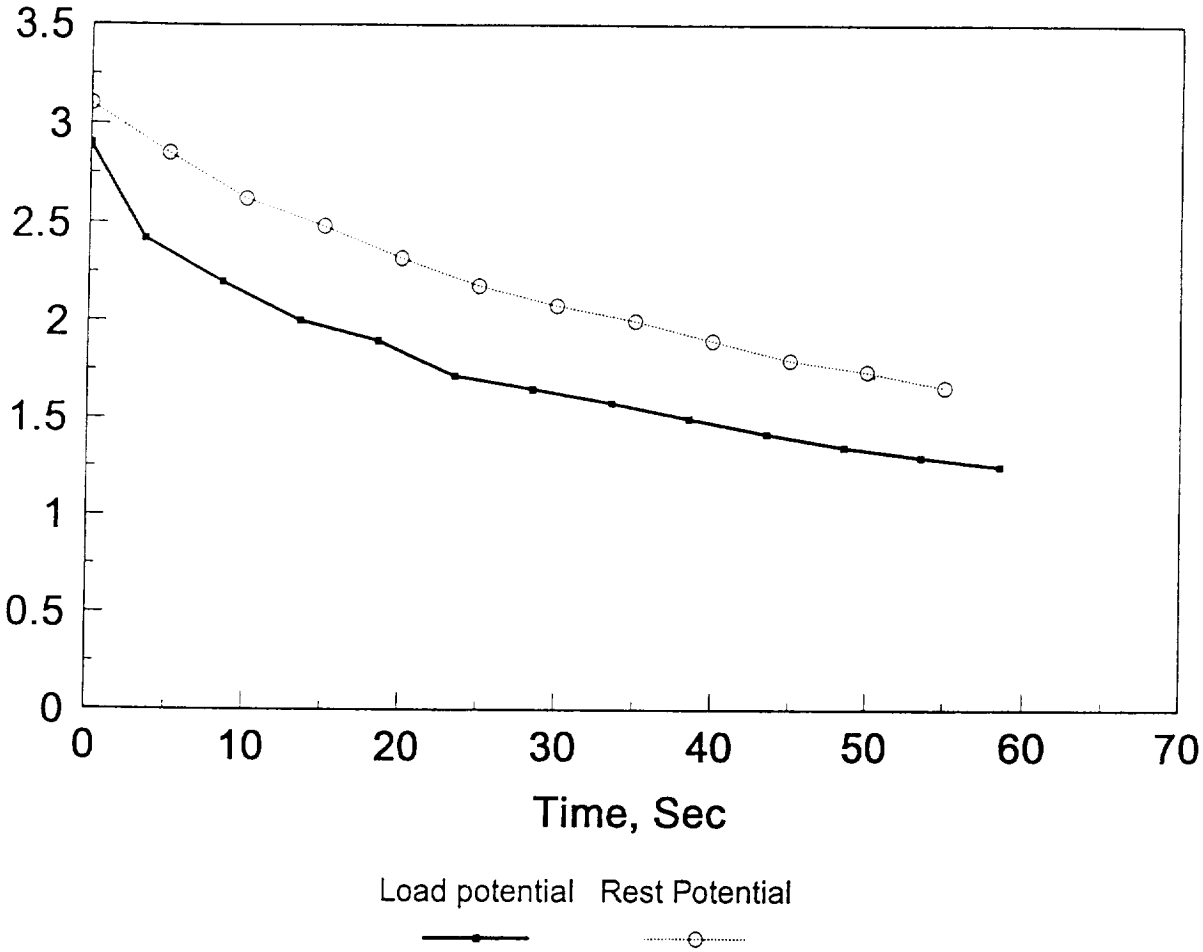
WS_2 additive gave good results. Even at relatively high discharge rates the delivered capacity does not decline significantly.



This work was oriented towards a pulse power battery application. This viewgraph shows the recorder trace for repetitive pulse discharges for a WS_2 additive containing cathode. The pulse current density is 1 A/cm^2 with the pulse duration of 3.5 seconds and 1.5 seconds between pulses.



The same figure is shown as loaded cell voltage as a function time. The profile is similar in shape to the steady state discharge curve. The rest potential between pulses behaves in a similar manner.



This viewgraph shows the pulse discharge profile for a WC - carbon cathode containing cell operating at 310 mA/cm^2, 3.5 second pulse width, 5 seconds/pulse.

RESULTS
Pulse Delivery Characteristics of Cathodes Li-Al Molten Salt Cells

Cathode Type	Pulse Duration sec.	Current Density A/cm^2	No. of Pulses to (Volts)	Power Density W/cm^2	Total Energy Joules
WC-C	3.5 (5 s/pulse)	0.248	12 (1.6)	0.64	340
		0.372	10 (1.4)	1.13	483
	8 (10s/pulse)	0.372	4 (1.5)	0.93	370
VO_x-C	8 (10s/pulse)	0.312	5 (1.2)	0.5	292
		0.625	7 (0.8)	0.9	488

This viewgraph shows the pulse delivery characteristics for various cathodes.

RESULTS
Pulse Delivery Characteristics of Cathodes Li-Al Molten Salt Cells

Cathode Type	Pulse Duration sec.	Current Density A/cm^2	No. of Pulses to (Volts)	Power Density W/cm^2	Total Energy Joules
Carbon	5	0.94	1	1.9	150
WS_2-C	3.5 (5 s/pulse)	0.312	14 (1.5)	0.7	439
		0.500	19 (1.5)	1.1	833
		0.625	19 (1.0)	1.4	812
		0.75	14 (0.5)	1.7	746
		1.00	10 (0.5)	2.0	619

This table exhibits the pulse delivery data for WS_2 - carbon cathode containing cells. For 625 mA/cm^2 current density pulses, the cell delivered a total energy of 812 joules in 19 pulses. At 1 A/cm^2 it exhibited a pulse power density of 2 W/cm^2.

Performance Projections

- Bipolar Cell stack 3" Diameter Based on Experimental Results
- 3.5 s Pulses, 0.625 A/sq.cm

Based on Improved Performance

- 8-s Pulses, 0.625 A/sq.cm above 1.50 V

For performance projection, 3" diameter bipolar cell stack is used with the experimental results obtained and performance improvement using 8-second duration pulses.

Performance Projection

System Level, 1 A/sq. cm

	Specific Power	Power Density
1 st pulse	3.2 kW/kg	5.5 kW/L
Av. Pow. 10 pulses	1.8	3.0

Specific power and power density are shown.

Performance Projection

System Level

	Specific Energy	Energy Density
Present	82 kJ/kg	140 kJ/L
Improved	145	248

Specific energy and energy density for the two cases are shown here.

CONCLUSIONS

- CARBON-BASED CHLORINE CATHODES WITH ADDITIVES
- SPECIFIC CATHODE CAPACITY 0.14 Ah/g-0.20 Ah/g
- REPETITIVE 3.5-S AND 8-S PULSES WITH 1.5 AND 2 SEC INTERVAL RESPECTIVELY
- POWER PERFORMANCE 1.5-2 W/sq.cm.
- PROJECTION TO THE SYSTEM LEVEL
  - 82 kJ/kg, 140 kJ/L - PRESENT RESULT
  - 145 kJ/kg, 248 kJ/L - IMPROVED RESULTS

This viewgraph summarizes the presentation.