STATUS OF JPL Li-ION CELL DEVELOPMENT PROGRAM

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1997 NASA BATTERY WORKSHOP
HUNTSVILLE, ALABAMA

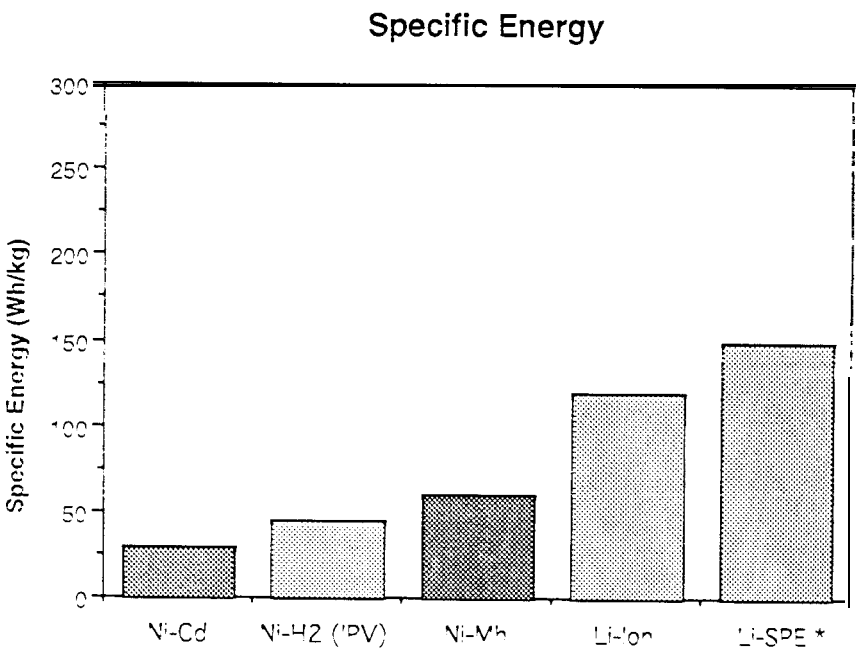
OUTLINE

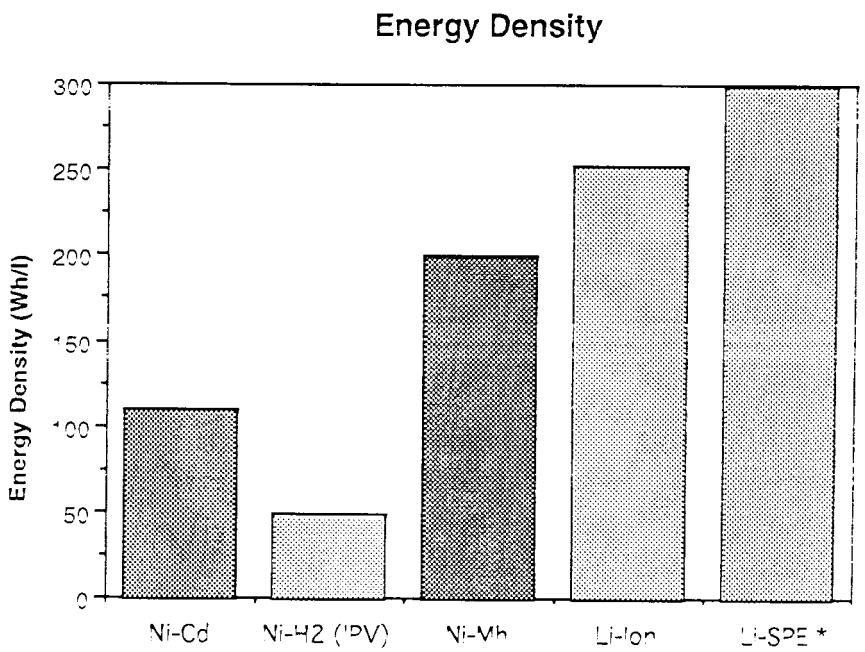
- JPL PROGRAM OVERVIEW
- LOW TEMPERATURE STUDIES
- CYCLE LIFE STUDIES
- DESTRUCTIVE PHYSICAL ANALYSIS (DPA) OF CYCLED CELLS
- PROTO TYPE CELL DEVELOPMENT
- SUMMARY OF ACCOMPLISHMENT

Li-Ion Cell Technology Benefits

Advantages		Comp. to SOA	Benefit to Mars Exploration Program
High specific energy	> 120 Wh/kg	2-3 x Ni-Cd/Ni-H2	Reduced mass and launch cost
High energy density	> 240 Wh/l	3-4 x Ni-Cd/Ni-H2	Reduced volume and launch cost
High operating voltage	3.6 V	3 x N -Cd/ Ni-H2	Improved reliability (fewer cells)
High coulombic efficiency	> 99%	> Ni-Cd	Reduced solar array size
Low self discharge	< 8%/ month	<<< Ni-Cd	Power system operation w/o solar array

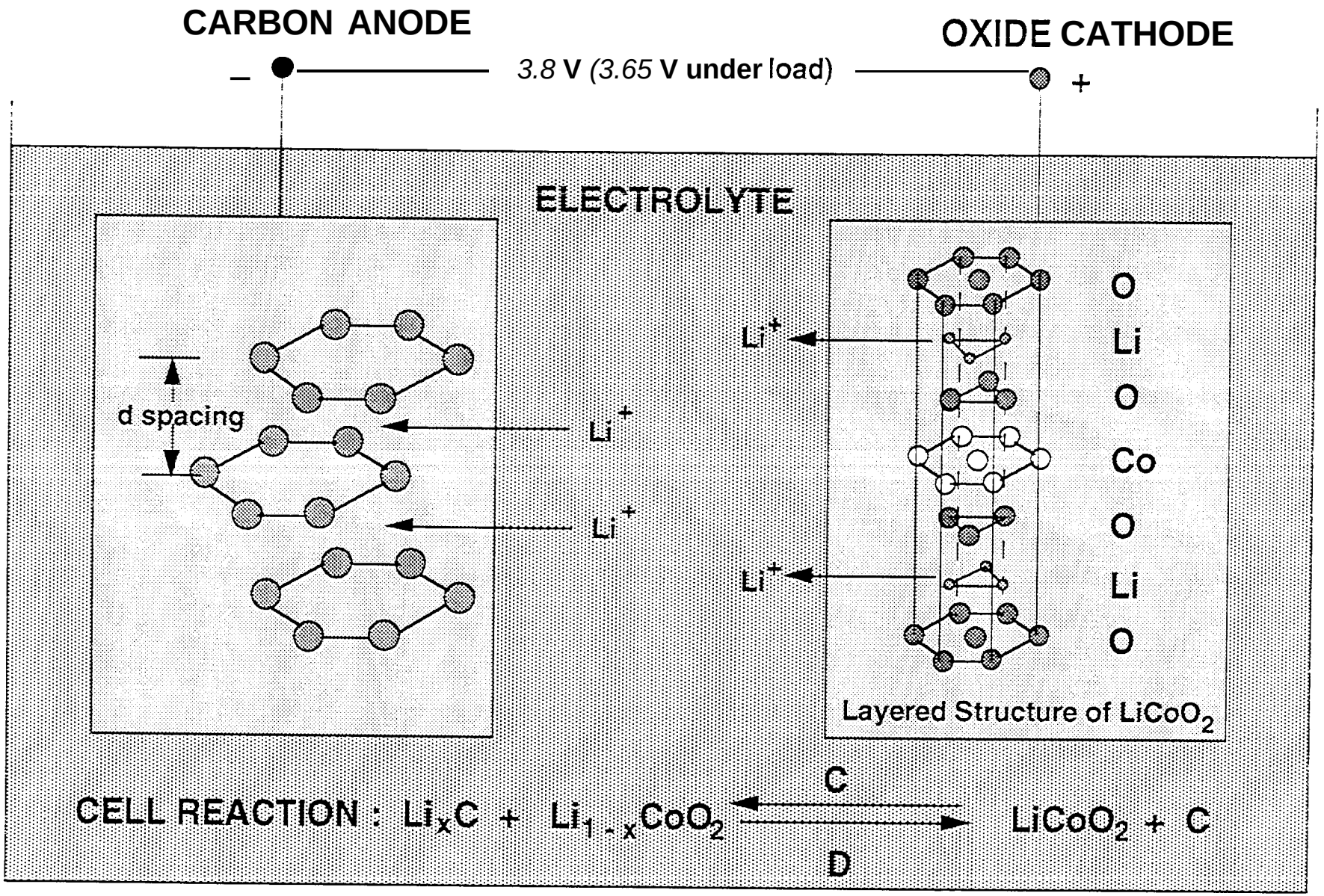
Performance Characteristics of Various Ce s/ Batteries





* Li-SPE projected

SCHEMATIC DIAGRAM OF A Li-ION CELL



Mission Battery Requirements

Mars Landers

- > 100 Wh/kg
  > 100 Wh/L
- Operating Temp. = -40° to 30°C
- 20 - 40 Amp•hour size

Rovers

- > 150 Wh/kg
  > 200 Wh/L
- Operating Temp. = -40° to 30°C
- 5 - 20 Amp•hour size
- > 500 cycles

Orbiters

- Operating Temp. = 0° to 30°C
- 20 - 40 Amp•hour size
- > 15,000 cycles (25% DOD)

Penetrators

Operating Temp. = -120° to -40°C
1 - 5 Amp•hour size

RECHARGEABLE LITHIUM BATTERY TASK

OBJECTIVES

- DEVELOP ADVANCED RECHARGEABLE LITHIUM ION CELLS FOR FUTURE MARS MISSIONS SUCH AS ORBITERS, LANDERS. ROVERS, AND ' PENETRATES.

PERFORMANCE TARGETS

> 100 Wh/Kg
> 200 Wh/L
-40 c to 30 c
1000 CYCLES (>60% DOD)
>15000 CYCLES @ 2570 DOD

TECHNICAL APPROACH

- IMPROVE LOW TEMP. PERFORMANCE
- IDENTIFY PARAMETERS WHICH AFFECT CYCLE LIFE PERFORMANCE
- DEMONSTRATE TECHNOLOGY AT 10 Ah LEVEL
- OPTIMIZE CHARGE CONTROL

Limitations of U.S. Lithium-Ion Battery Technology

Cell Level Issues

- Small capacity cells (I-5 Amp•hr)
- Limited cycle life
- Limited operating temperature range (-1 O to 40 C)
- Sensitive to overcharge and discharge

Battery Level Issues

- Cell uniformity lacking
- Charge mangement
- Limited data base at the battery level
- Safety

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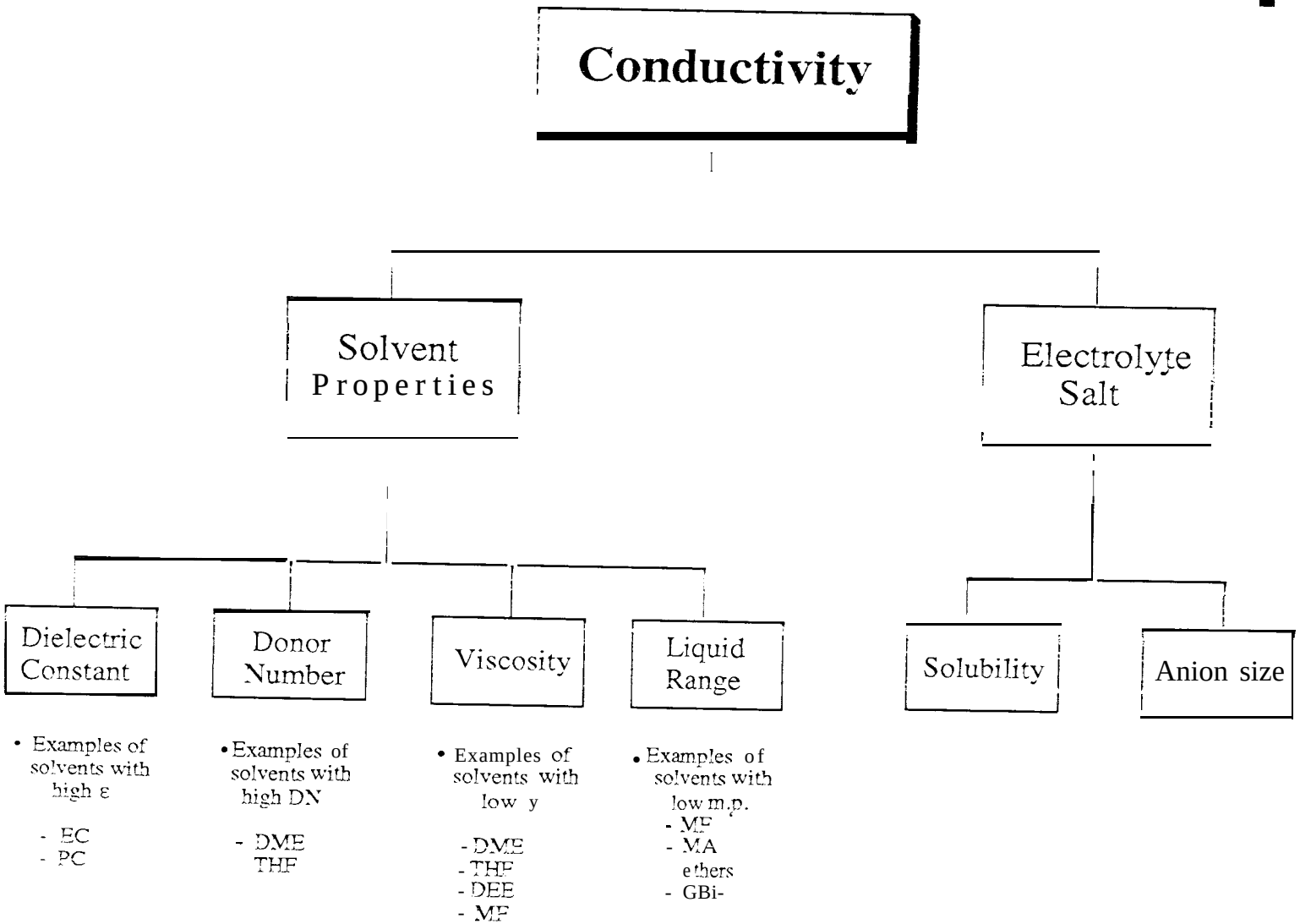
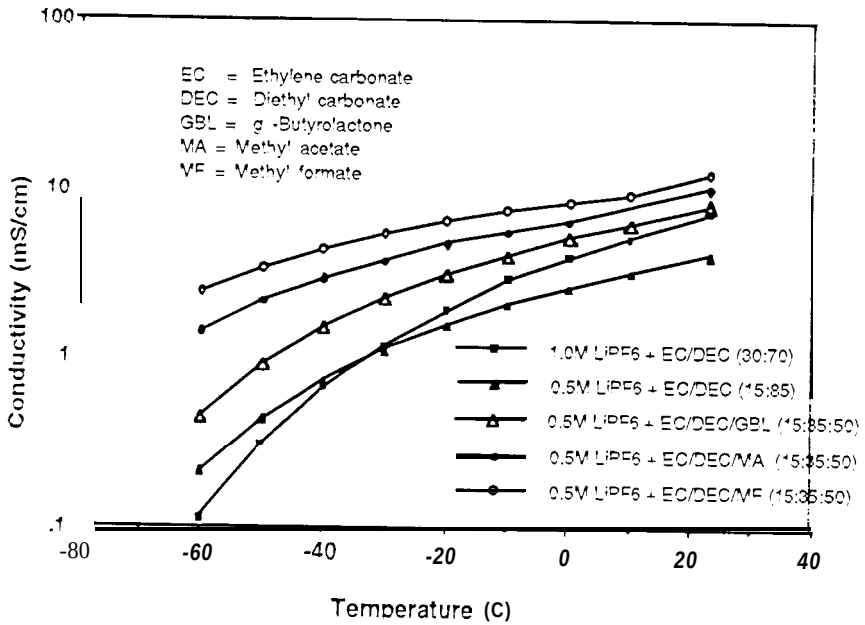
Technical Issues and Research & Development Strategies

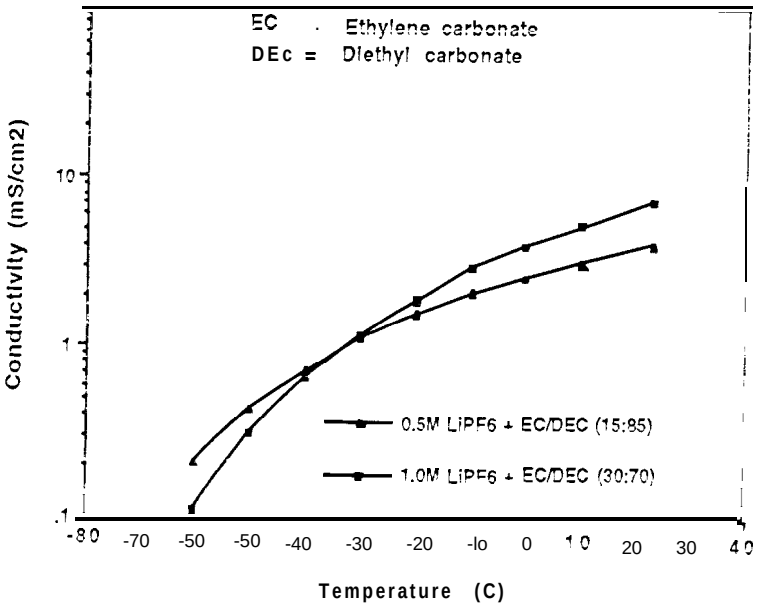
Issues	Approaches
.Improve Low Temperature Performance	• Low temp.conducting electrolytes .Electrode materials with high Li^+ diffusivity " Thin electrodes .Type of separator
.Improve Cycle Life	.High stability electrolytes .Electrode materials with high reversibility Ceil design - Electrode capacity ratios - Cell pack tightness - Type of separator
.Increase Specific Energy	• High specific energy cathodes .High specific energy anode materials . Lightweight hardware
.Increase Capacity	.Effective electrode fabrication methods .Effective quality controls
.Establish Charge Control	• Charge methods " Voltage limits .Operating temperature " Charge current
.Establish Database Management	.Accelearated LEO testing • Acceleratied GEO testing " 100 % DOD testing .Establish self-discharge characteristics .Determine effect of temperature upon life

Li-Ion Low Temperature Electrolyte Selection: Factors Which influence Conductivity



Low Temperate Electrolyte Conductivity Studies: Evaluation of EC-Based Electrolyte

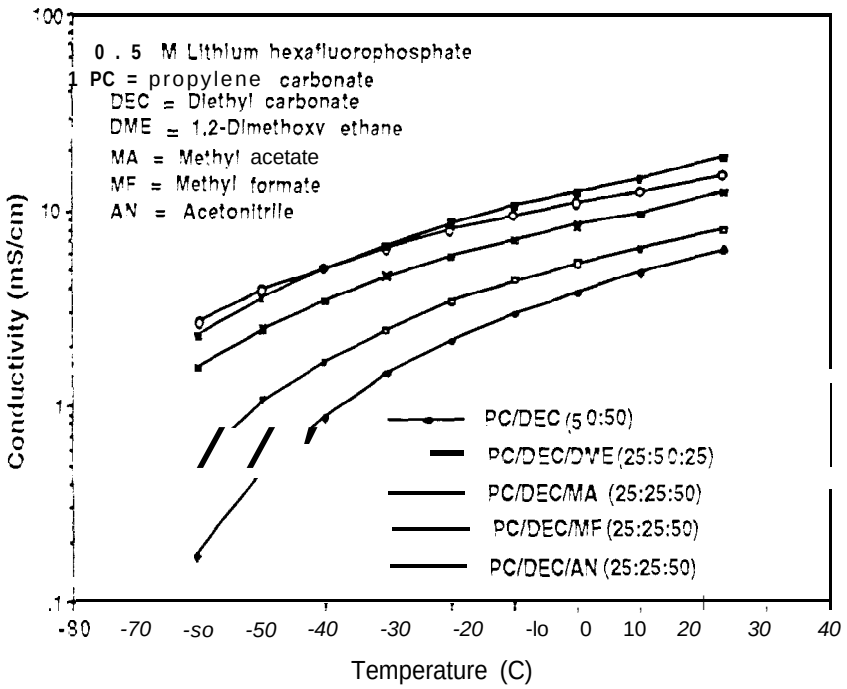


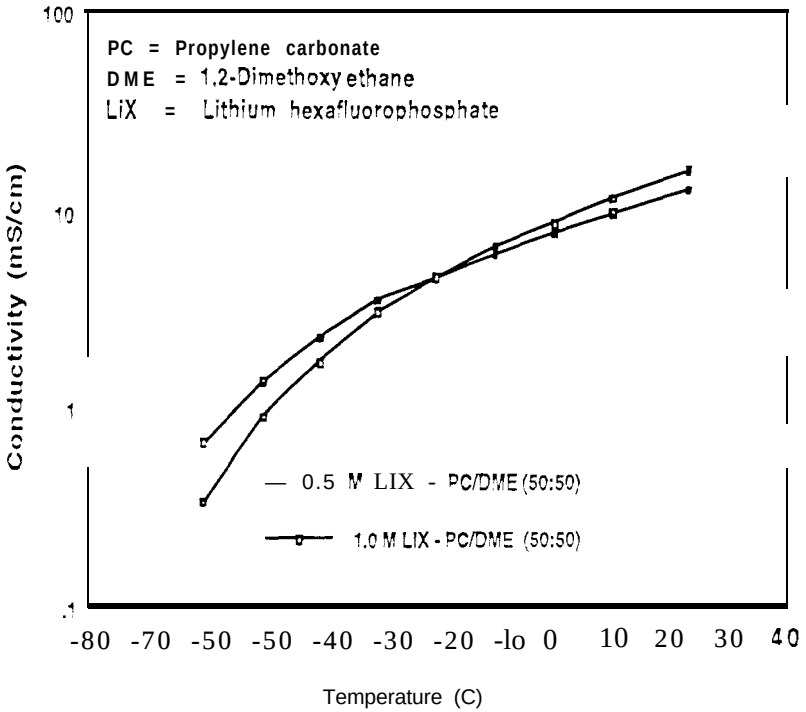


- Higher conductivites are observed at low temperatures with electrolyte solutions possessing lower salt and **EC** concentrations.

- The addition of low viscosity co-solvents dramatically increases the conductivty at lower temperatures.

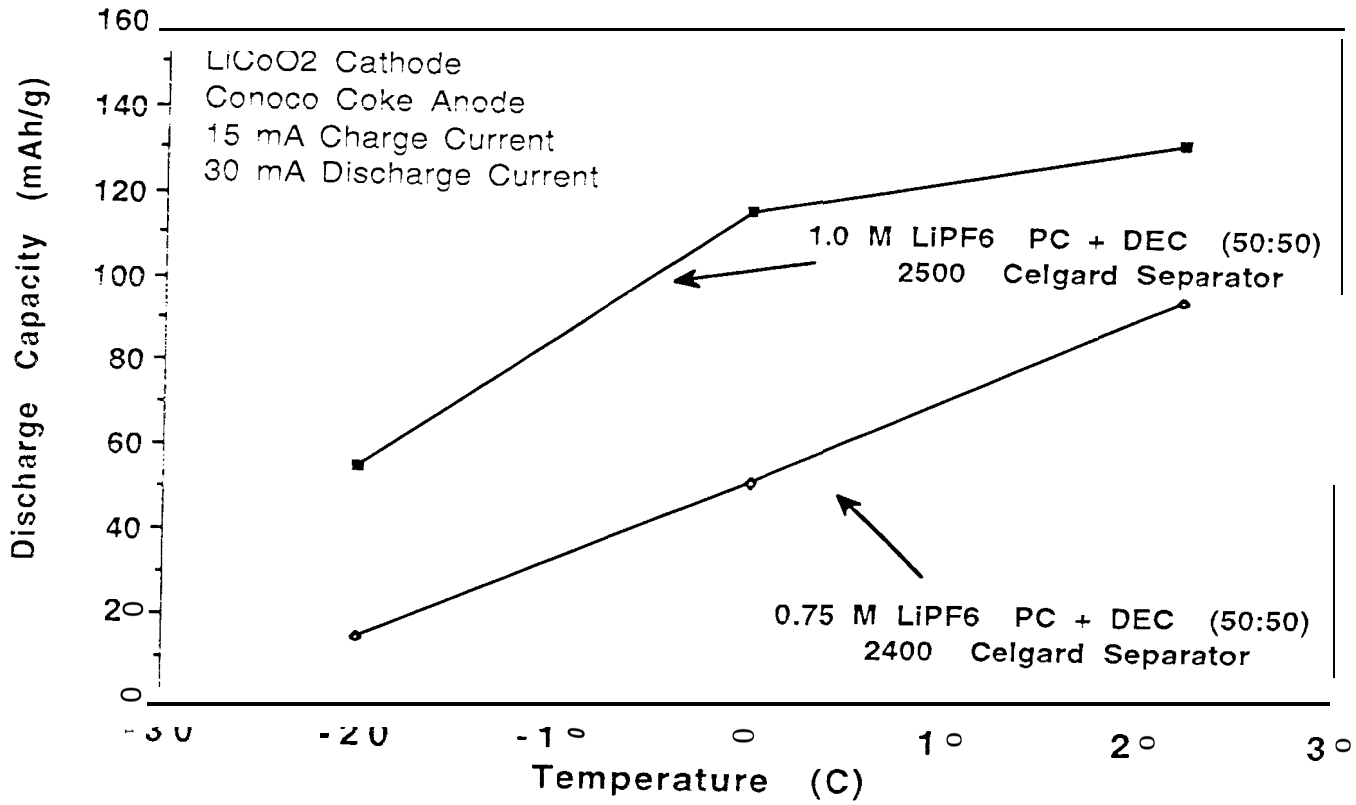
Low Temperature Electrolyte Conductivity Studies: Evaluation of PC-Based Electrolytes





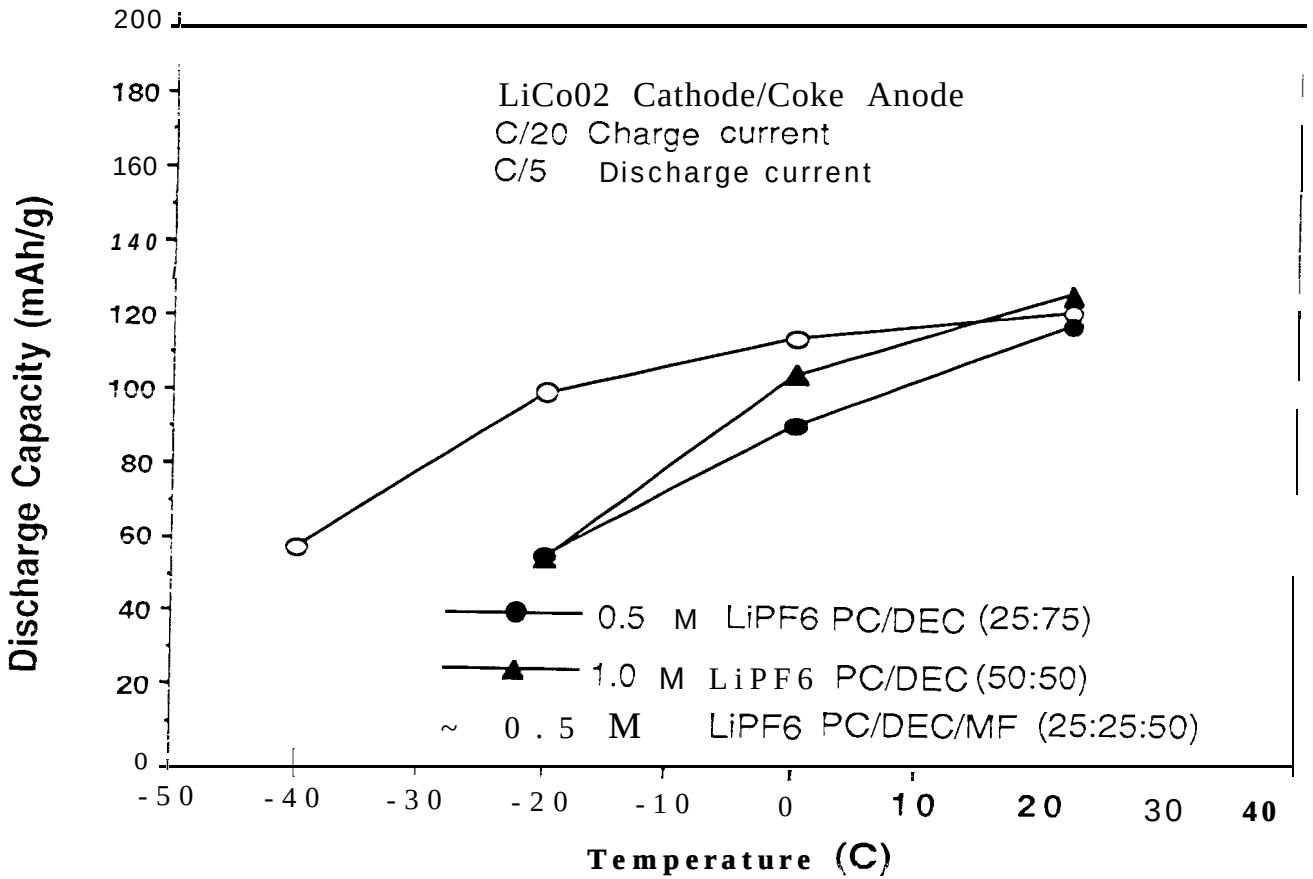
- **Lower electrolyte salt concentrations result in more highly conducting solutions at low temperatures.**
- **Low viscosity electrolyte solutions have higher conductivity at low temperatures (accomplished with low salt and PC concentrations and/or the addition of low viscosity additives).**

Low Temperature Performance of JPL Lithium-Ion Cells
Effect of Separator Porosity

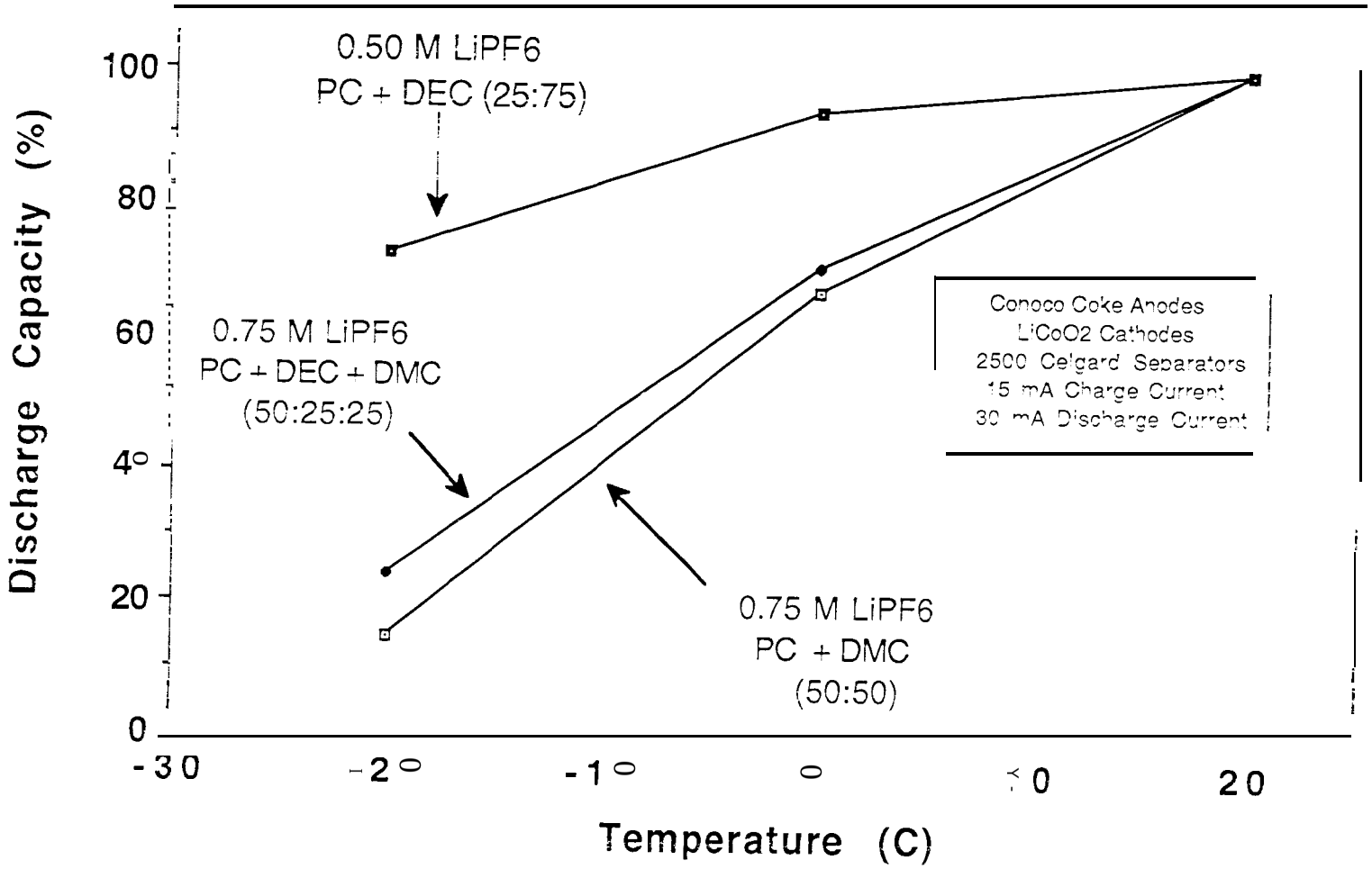


- Discharge characteristics of cells fabricated with the high porosity separator material (Celgard 2500) were superior at all temperatures to cells possessing the lower porosity material.

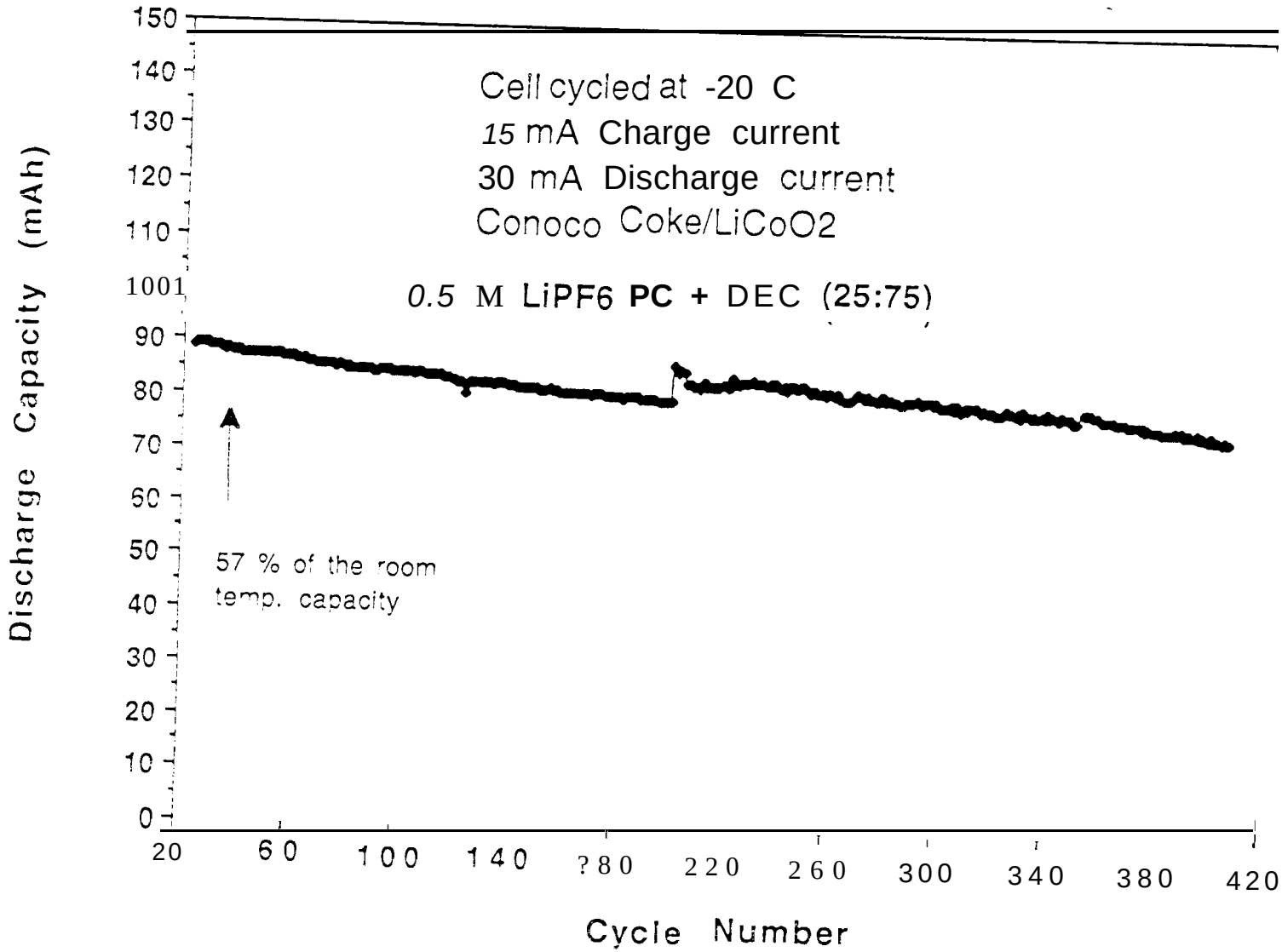
Low Temperature Performance of Lithium-Ion Cells Discharge Characteristics of PC-Based Electrolytes



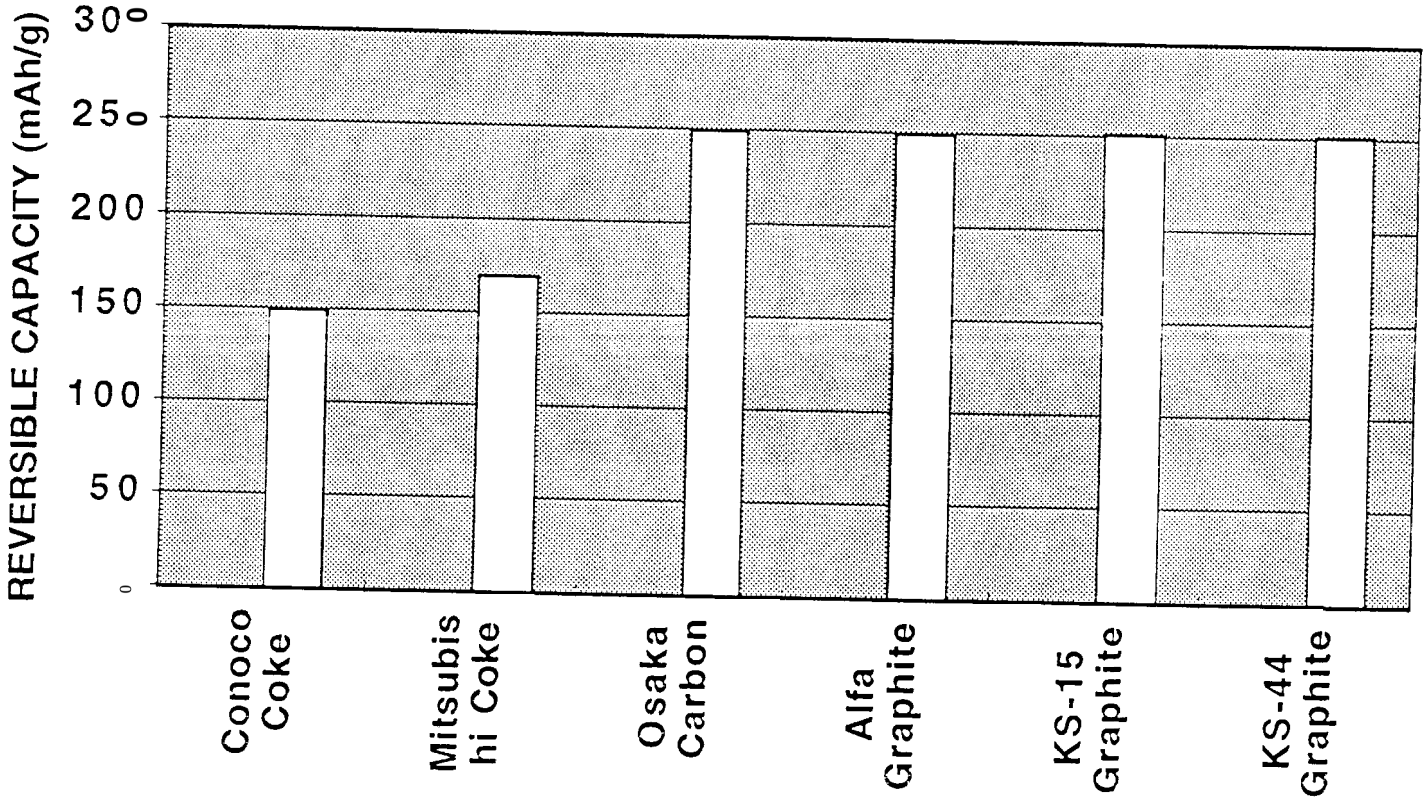
Evaluation of the Low Temperature Performance of Lithium-Ion Cells with PC-Based Electrolytes



Performance of JPL Low Temperature Li-Ion Cells



EVALUATION OF CARBON ANODE MATERIALS (FULL CELL STUDIES)



irreversible and Reversible Capacities of PC-Based Electrolytes with Conoco Coke Anodes

Electrolyte	Irreversible Capacity (mAh/g)	Reversible Capacity (mAh/g)
PC + DEC (50:50) 1.0 M $LIPF_6$	114	137
PC + DEC (25:75) 0.5 M $LIPF_6$	118	135
PC + DEC + MF (25:25:50) 0.5 M $LIPF_6$	140	123
PC+ DEC -I- MA (25:25:50) 0.5 M $LIPF_6$	145	83
PC + DEC + GBL (25:25:50) 0.5 M $LIPF_6$	255	5
PC + DEC + DME (25:25:50) 0.5 M $LIPF_6$	122	82

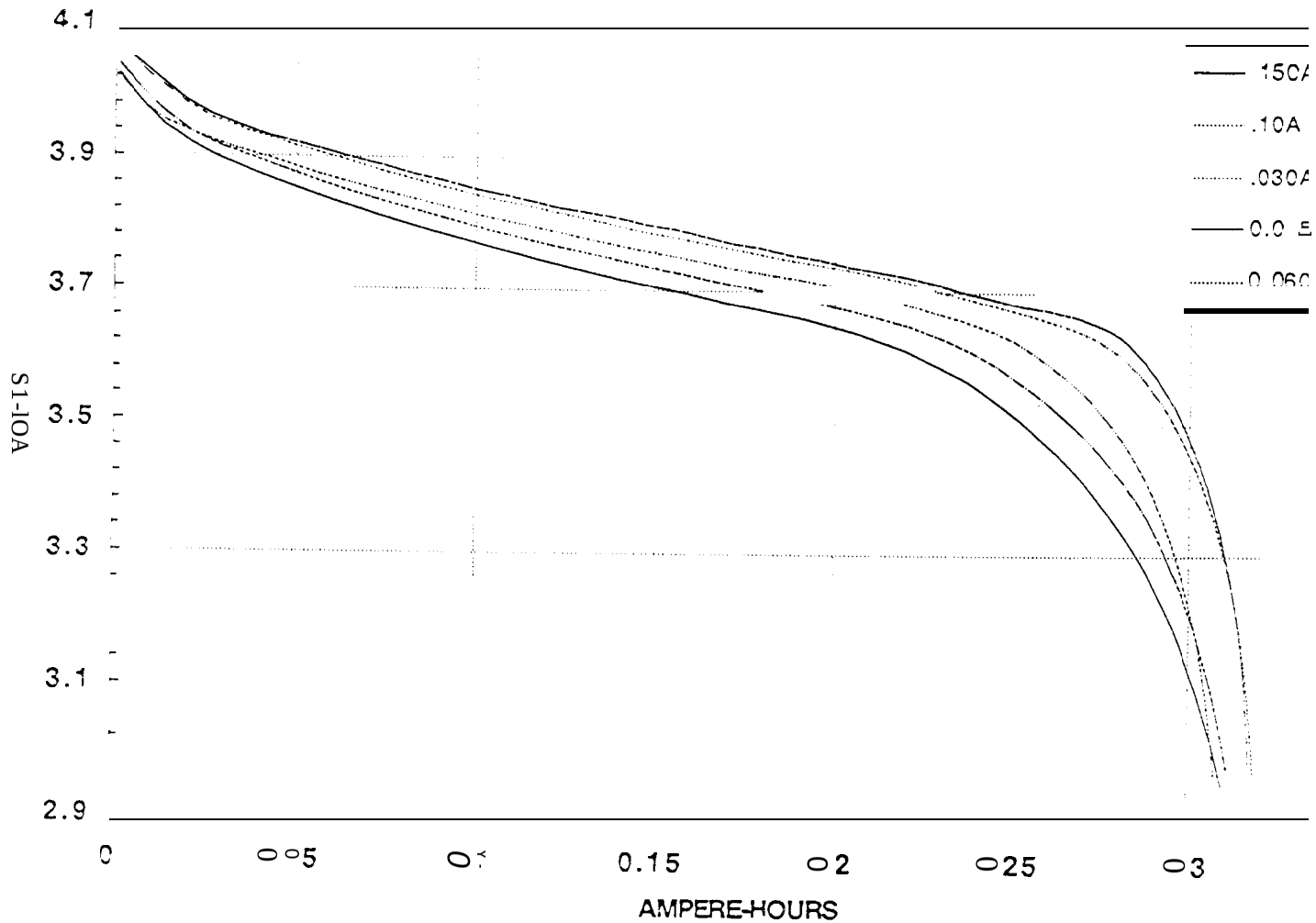
Irreversible and Reversible Capacities of EC-Based Electrolytes with Alfa Graphite

Electrolyte	Irreversible Capacity (mAh/g)	Reversible Capacity (mAh/g)
EC + DMC (50:50) 1.0 M $LiPF_6$	113	150
EC + DEC (30:70) 1.0.34 $LiPF_6$	58	240
EC + DMC (30:70) 1.0 M $LiPF_6$	60	250
EC + DEC + DMC (34:33:33) 1.0 M $LiPF_6$	58	253
EC+ DEC + MF (35:15:50) 0.5 M $LIPF_6$	60	252
EC + DEC -L MA (35:15:50) 0.5 M $LIPF_6$	32	285
EC + DEC + DME (35:15:50) 0.5 M $LIPF_6$	257	58
EC+ PC + DEC + MA (35:15:50) 0.5 M $LIPF_6$	122	193
EC + PC + DEC + GBL (35:15:50) 0.5 M $LIPF_6$	146	148

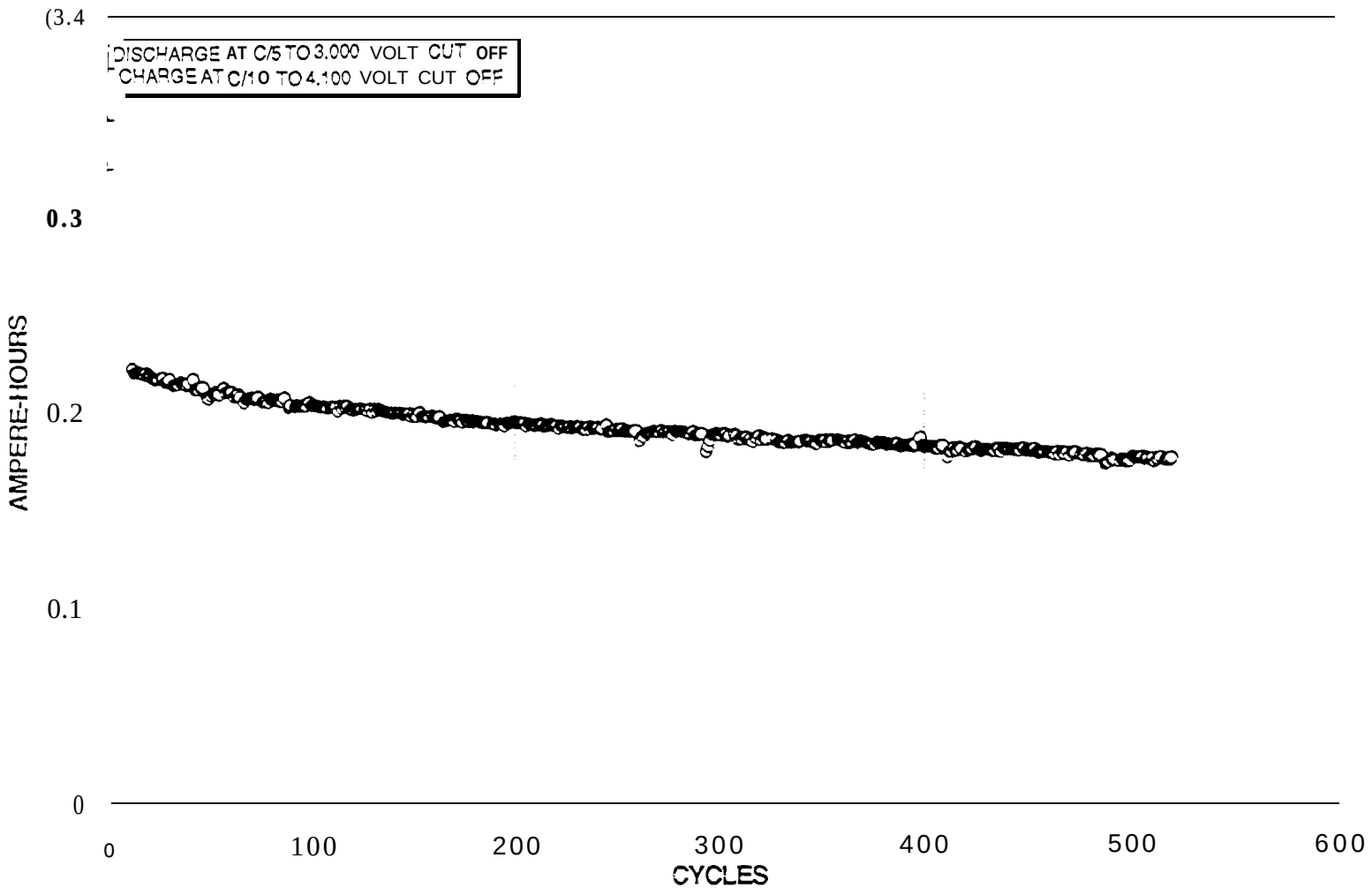
EFFECT OF ELECTRODE WEIGHT RATIO ON CELL PERFORMANCE

WEIGHT RATIO	REV. CAPACITY (mAh/g)	CAP. FADE RATE (% per cycle)
2.5	252	0.06-0.09
2.8	272	0.107
3.1	298	0.125
3.4	306	0.16

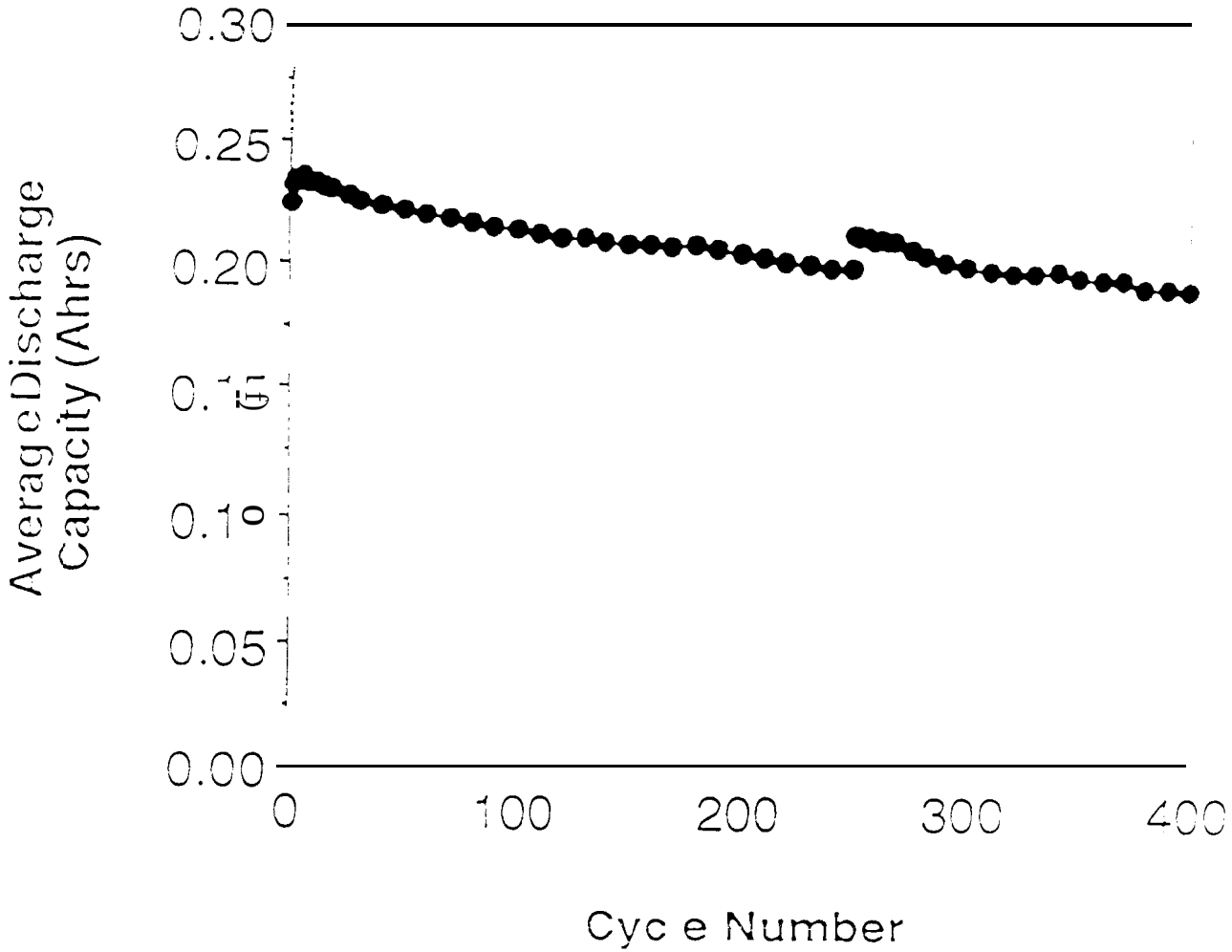
RATE CAPABILITY OF JPL Li-ION CELL



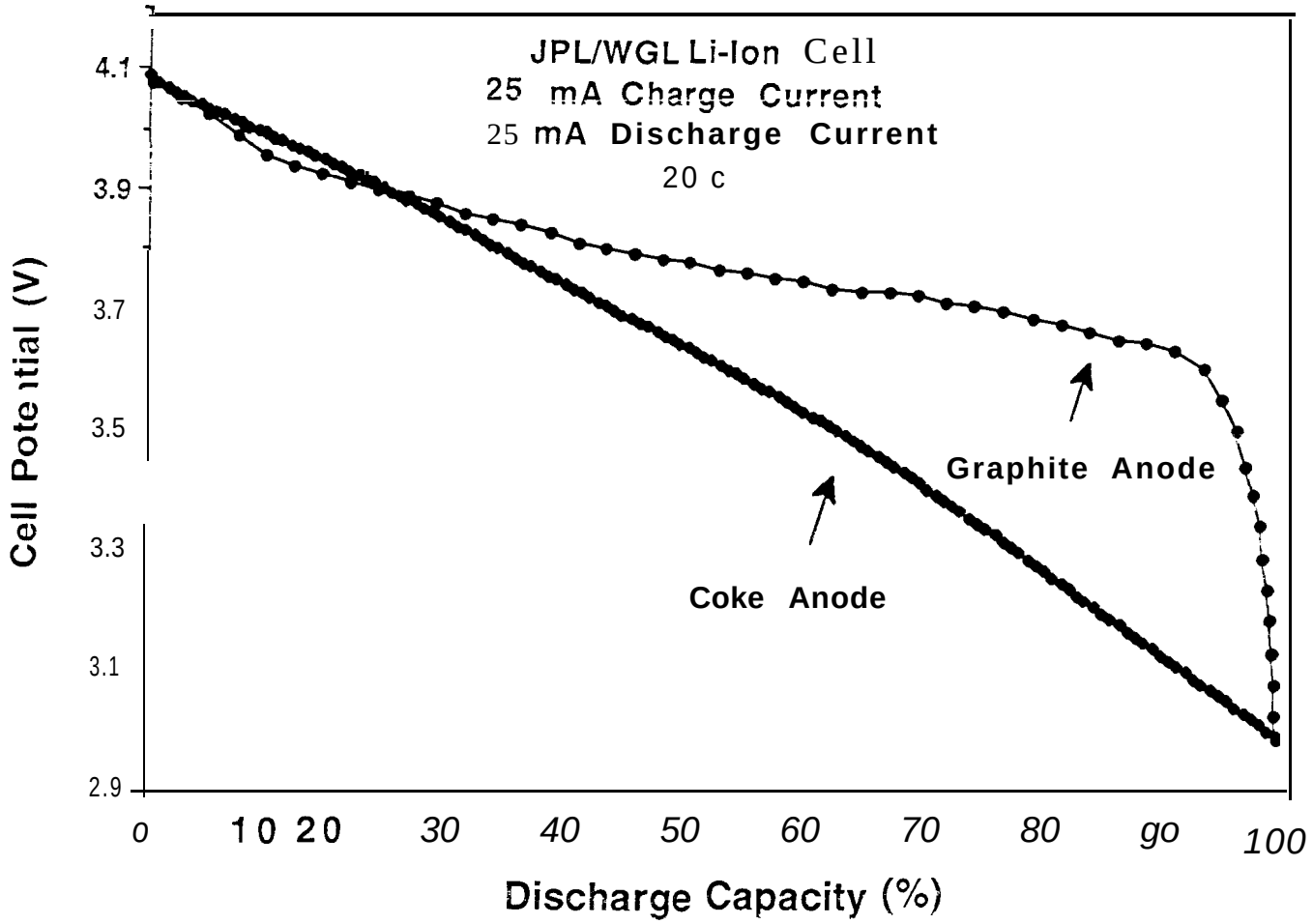
CYCLE LIFE PERFORMANCE OF Li-ION CELL CONTAINING GRAPHITE ANODE



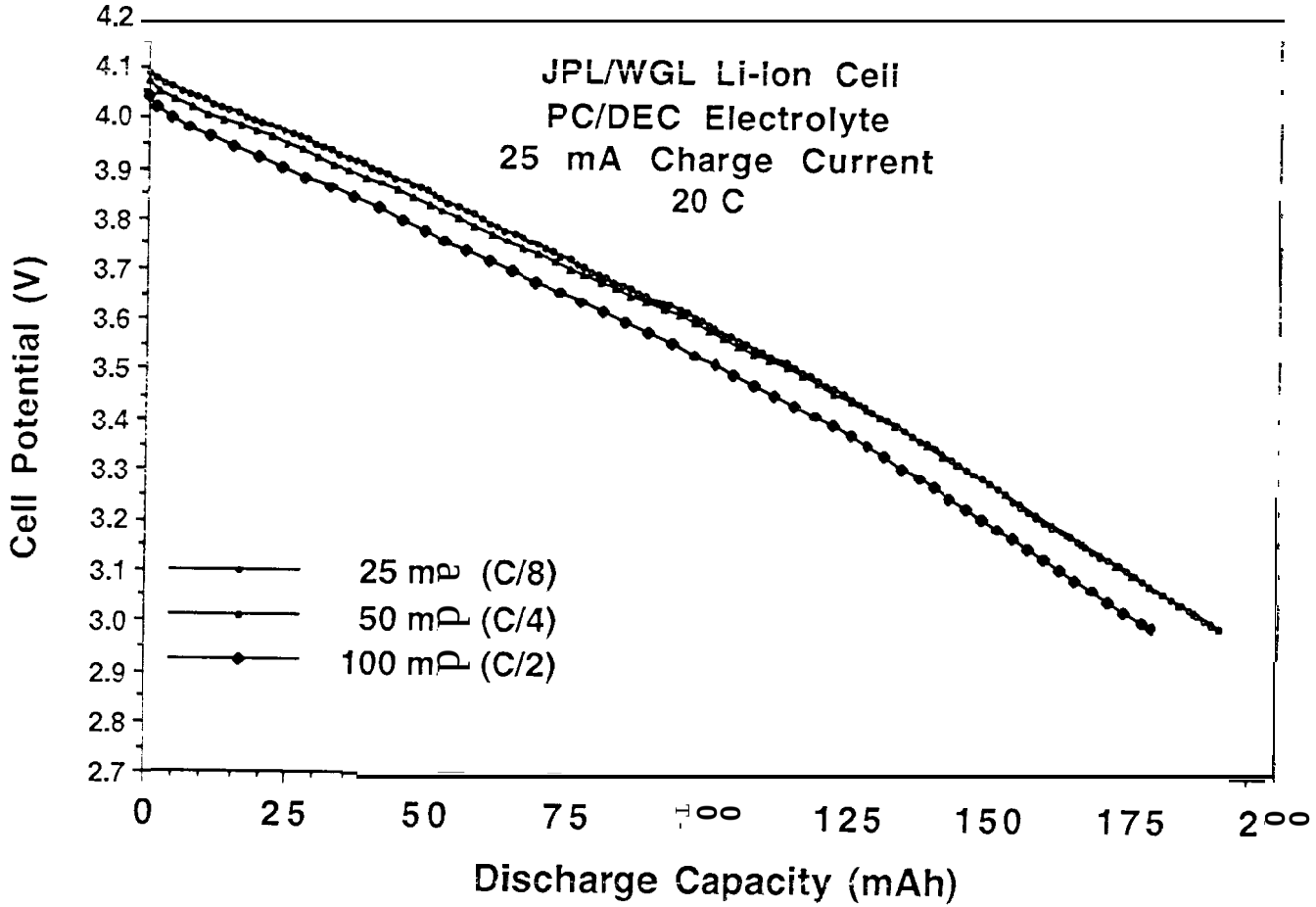
CYCLE LIFE PERFORMANCE OF Li-ION CELL CONTAINING COKE ANODE



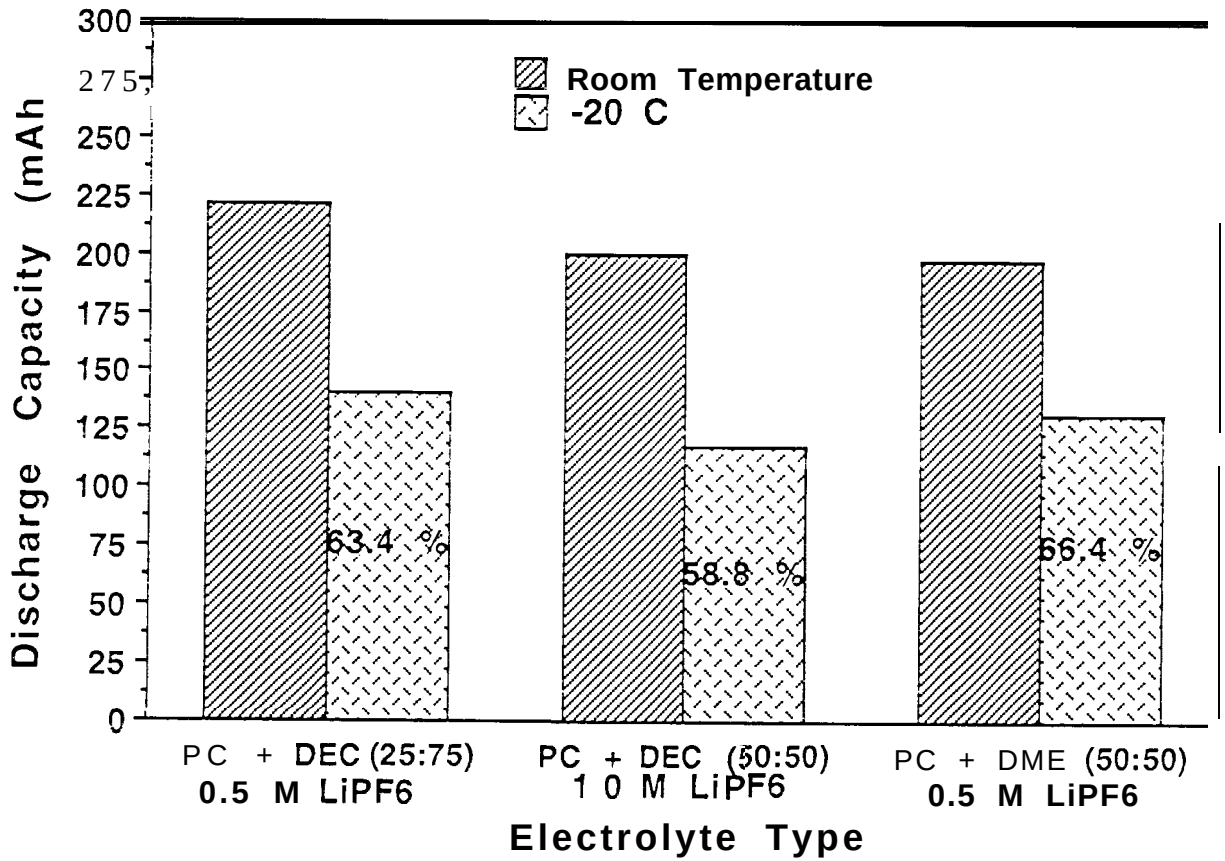
Performance of JPL/WGL Li-Ion Cells: Discharge Characteristics of Coke vs Graphite Anodes



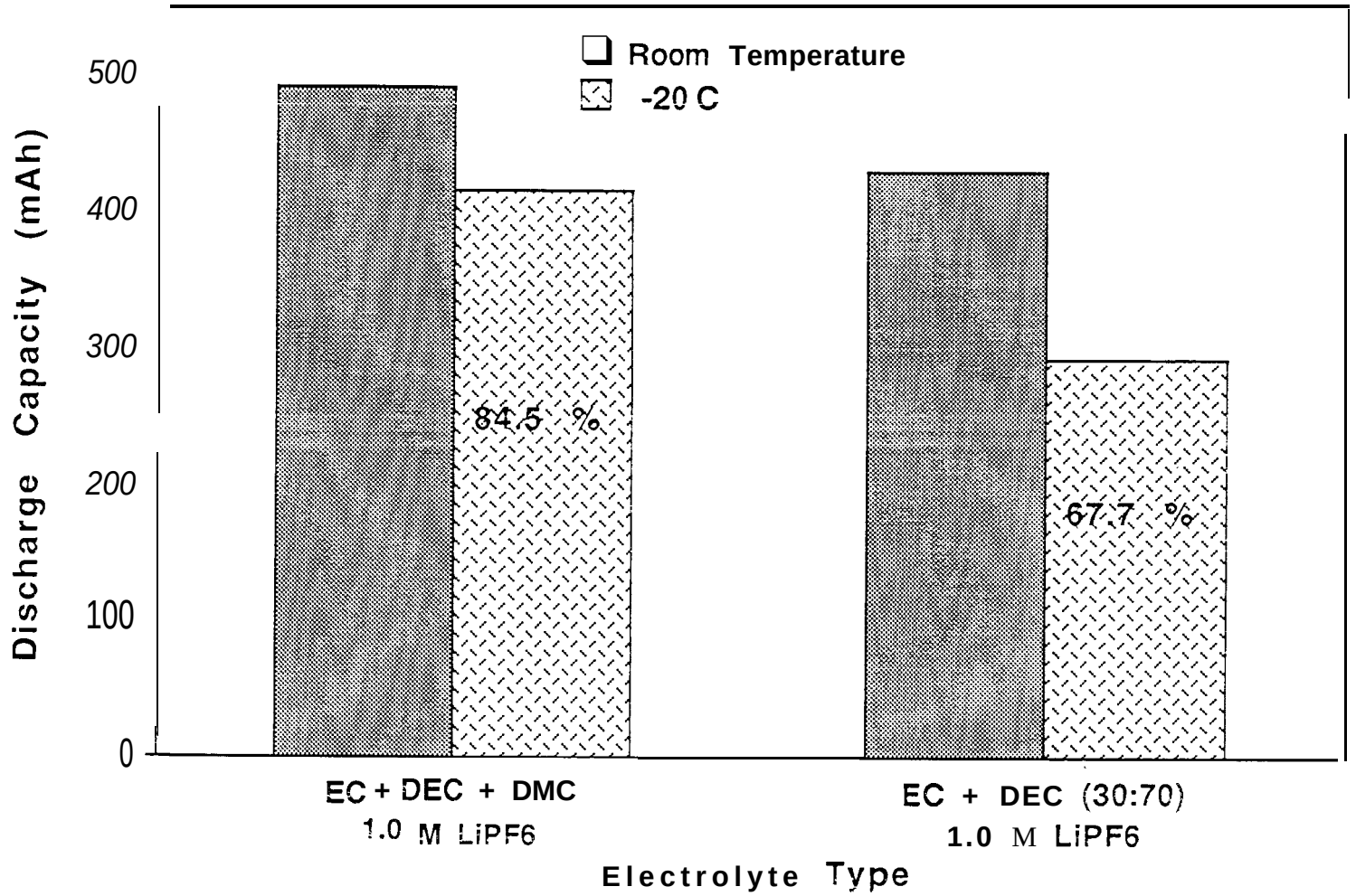
Performance of JPL/WGL Li-Ion Cells
Evaluation of Rate Capability



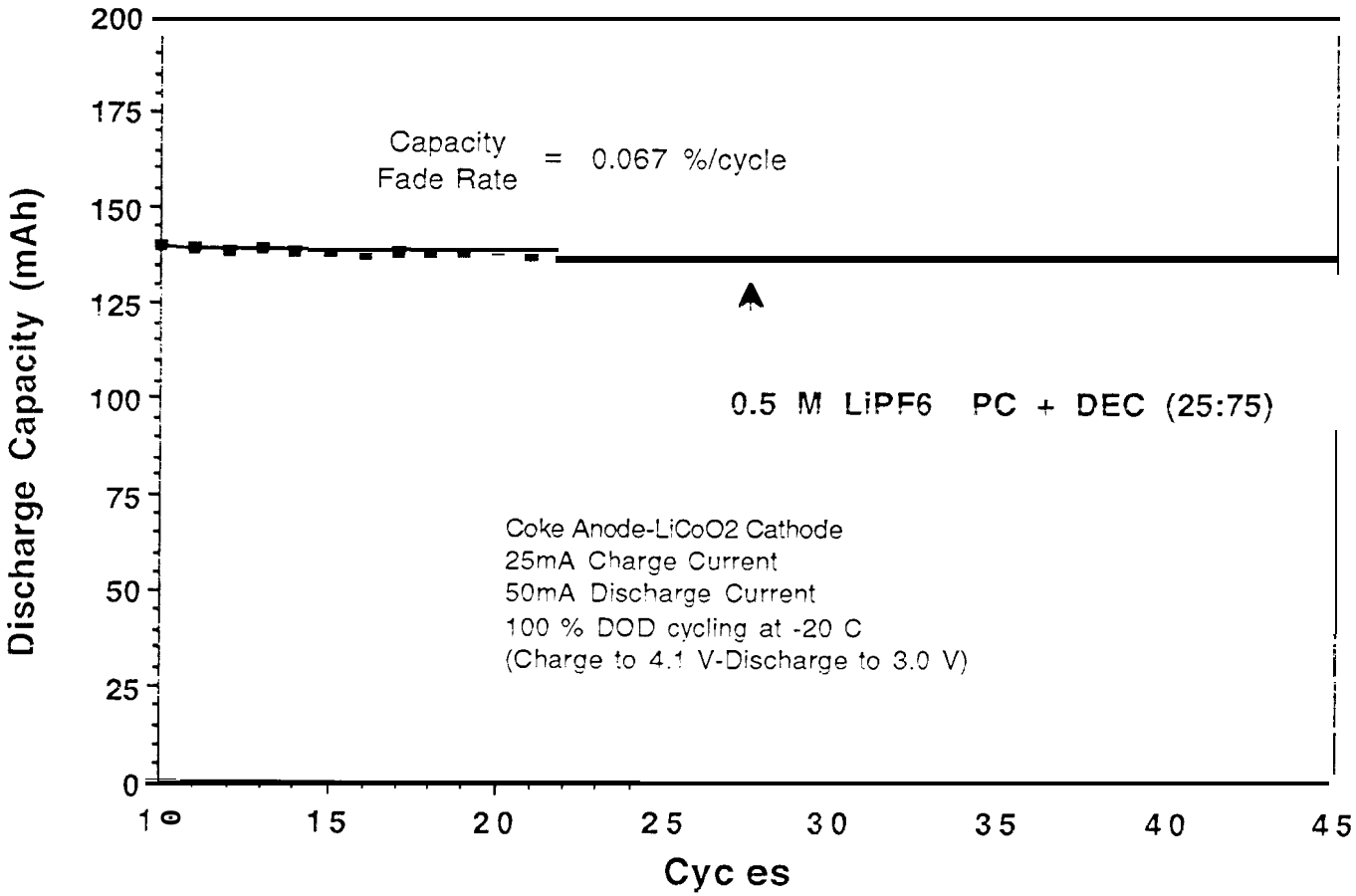
Low Temperature Performance of JPL/WGL Lithium-ion Cells: Discharge Characteristics as a Function of Temperature



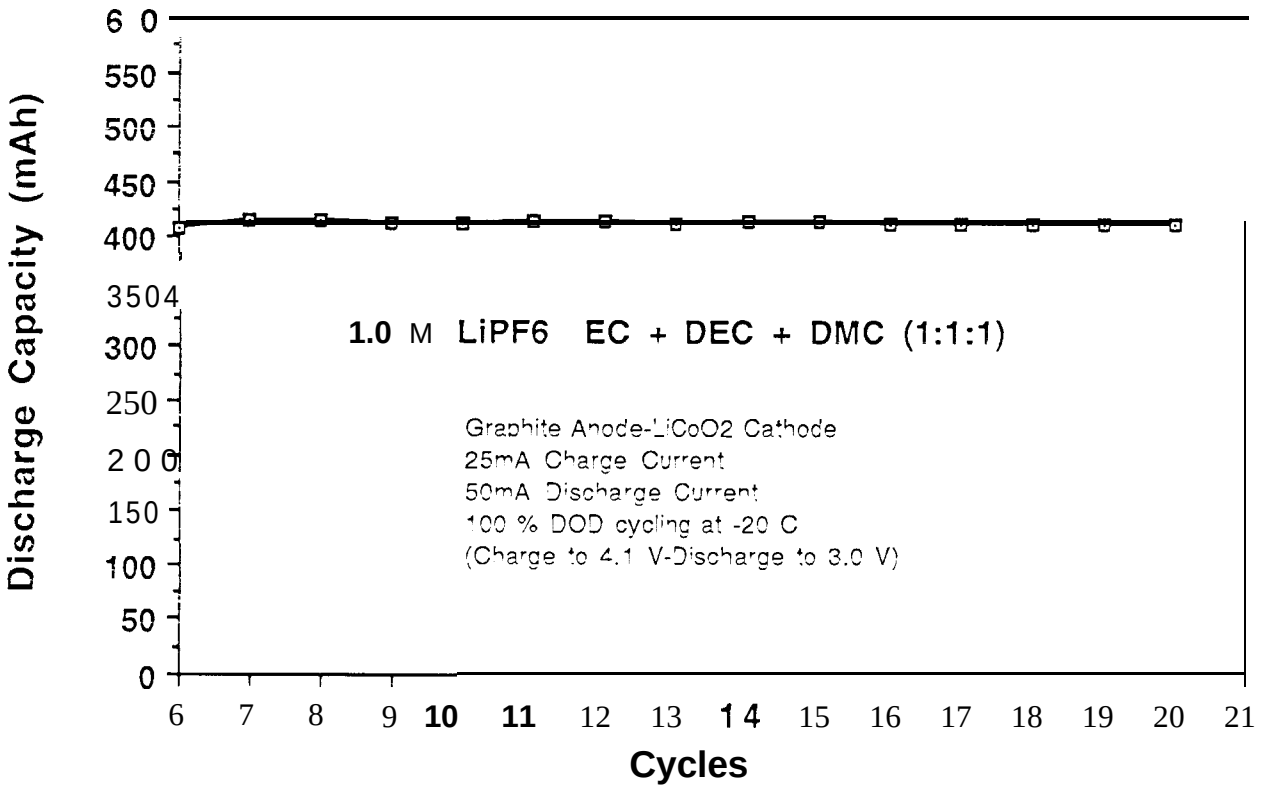
Low Temperature Performance of JPL/WGL Lithium-Ion Cells: Discharge Characteristics as a Function of Temperature



Low Temperature Performance of JPL/WGL Lithium-Ion Cells: Cycle Life Performance at -20C



Low Temperature Performance of JPL/WGL Lithium-Ion Cells: Cycle Life Performance at -20 C



- Capacity Fade Rate = 0.05" % per cycle
- Cell delivered 84.5 % of the room temperature capacity at -20 c
- Cell delivered 77.5 Wh/Kg at -20 C

FAILURE MODES OF RECHARGEABLE Li-ION CELLS

(1) INTERNAL SHORTING

(2) CAPACITY DECLINE

SUMMARY OF DPA RESULTS

(1) EDX ANALYSIS

- COPPER ON ANODE AND CATHODE
- COBALT ON ANODE
- COPPER ON BOTH ANODE AND CATHODE SEPARATORS
- SILICON AND ALUMINUM ON ELECTRODES

(2) X-RAY DIFFRACTION

- CATHODE STRUCTURE SLIGHTLY CHANGED
- NO OBVIOUS CHANGE IN GRAPHITE C-SPACING

(3) MICROSTRUCTURAL

- ANODE CURRENT COLLECTOR (Cu) EXHIBITS CORROSION
- CATHODE CURRENT COLLECTOR (Al) EXHIBITS CORROSION
- SEPARATOR BECOMES COLORED
- FILM COVERING SURFACE OF BOTH ELECTRODES

(4) AC IMPEDANCE MEASUREMENTS

- ELECTROLYTE RESISTANCE REMAINS THE SAME
- CHARGE TRANSFER RESISTANCE OF ELECTRODE INCREASES WITH CYCLING
    * CATHODE INCREASE MORE THAN ANODE

SUMMARY OF ACCOMPLISHMENTS

(1) IDENTIFIED ELECTRODE MATERIALS AND ELECTROLYTES THAT CAN PROVIDE

- SPECIFIC CAPACITY > 250 mAh/g
- CAPACITY FADE RATE ~ 0.06% PER CYCLE

(2) DESIGNED AND FABRICATED CELLS THAT EXHIBITED

- SPECIFIC ENERGY >105 Wh/Kg
- ENERGY DENSITY >240 Wh/L
- CYCLE LIFE >500 CYCLES
- OPERATE TEMP.: -20-60 C

(3) IDENTIFIED ELECTRODE MATERIALS AND ELECTROLYTES WHICH PROVIDE IMPROVED LOW TEMPERATURE PERFORMANCE OF Li-ION CELLS

- DEMONSTRATED SPECIFIC ENERGY >75 Wh/Kg AT -20 C
- DEMONSTRATED >400 CYCLES AT -20 C @ 100% DOD
- PC-BASED CELL DELIVERED > 60% OF RT CAPACITY AT -20 C
- EC-BASED CELL DELIVERED > 80% OF RT CAPACITY AT -20 C
- CAPACITY FADE RATE AS LOW AS 0.0694 PER CYCLE
- IDENTIFIED ELECTROLYTES CAPABLE OF OPERATION AT -40 C

(4) PERFORMED DESTRUCTIVE PHYSICAL ANALYSIS ON CYCLED IN-HOUSE AND COMMERCIAL Li-ION CELLS AND IDENTIFIED A NUMBER OF FAILURE MODES AND MECHANISMS.