Li-ION CELL DEVELOPMENT FOR LOW TEMPERATURE APPLICATIONS

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THE 196TH MEETING OF THE ELECTROCHEMICAL SOCIETY
HONOLULU, HAWAII
OCT. 17-22, 1999
(1) BACKGROUND

(2) EXPERIMENTAL

(3) RESULTS AND DISCUSSIONS

- SELECTION OF ELECTROLYTES
- EVALUATION OF CATHODE PERFORMANCE
- EVALUATION OF ANODE PERFORMANCE
- LI DIFFUSIVITY IN CARBON
- EFFECT OF PARTICLE SIZE

(4) SUMMARY
PROGRAM OVERVIEW

(1) GOAL: DEVELOP LI-ION TECHNOLOGY FOR FUTURE MARS MISSIONS.

(2) PERFORMANCE TARGETS:  > 100 (WH/KG)
    500 - 1000 (CYCLES)
    -40 C ~ +60 (C)
    5 YEAR CALENDAR LIFE
    RATE CAPABILITY C/2 - C/10

(3) TECHNICAL APPROACH:
    - IDENTIFY ADVANCED ELECTRODE MAT.
    - IDENTIFY E'LYTE TO IMPROVE LT OPERATION
    - IDENTIFY KEY DESIGN PARAMETERS THAT
      CONTROL CELL PERFORMANCE

(4) NEAR TERM MISSIONS:
    - MARS 2001 LANDER
    - MARS 2003 LANDER AND ROVER
    - MARS 2005 MARS SAMPLE RETURN MISSION

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**OBSERVATION OF ELECTROLYTES AFTER FOUR DAYS STORAGE AT SPECIFIC TEMPERATURES**

<table>
<thead>
<tr>
<th>Composition</th>
<th>-30 C</th>
<th>-35 C</th>
<th>-40 C</th>
<th>-42.5 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC:DEC:DMC (1:1:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0M LiPF6</td>
<td>Liquid</td>
<td>Frozen</td>
<td>Frozen</td>
<td>Frozen</td>
</tr>
<tr>
<td>0.9M LiPF6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC:DEC:DMC:EMC (3:5:4:1)</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>0.8M LiPF6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC:DEC:DMC:EMC (3:5:4:2)</td>
<td>Liquid</td>
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<td>0.8M LiPF6</td>
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EC=Ethylene Carbonate, DEC=Diethyl Carbonate, DMC=Dimethyl Carbonate, EMC=Ethyl Methyl Carbonate, PC=Propylene Carbonate
CYCLING PERFORMANCE OF CELLS CONTAINING VARIOUS ELECTROLYTES

- H1 = 1.0M LiPF6/EC+DEC+DMC (1:1:1)
- H2 = 0.9M LiPF6/EC+DEC+DMC+PC (3:3:3:1)
- H3 = 0.8M LiPF6/EC+DEC+DMC+EMC (3:5:4:1)
- H4 = 0.8M LiPF6/EC+DEC+DMC+EMC (3:5:4:2)
PERFORMANCE OF CATHODE AT VARIOUS TEMP.

I = 0.197 (mA/cm²)

LiCo₀.₂Ni₀.₈O₂

Potential vs. Li (Volts)

-40 C 46%
-30 C 60%
-20 C 70%
+20 C

Capacity (Ah)

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CATHODE CHARGE & DISCHARGE PROFILES AT -40°C

Potential vs. Li (Volts)

Capacity (Ah)

LiCo0.2Ni0.8O2
Temp = -40°C

Li out I = 40 (mA)
Li out I = 20 (mA)
Li in I = 10 (mA)
Li in I = 20 (mA)
Li DE-INTERCALATION OUT OF GRAPHITE

I = 0.22 (mA/cm²)
EC+DEC+DMC+EMC (3:5:4:1)

Potential vs. Li (Volts)

-40 C, 87%
-30 C, 97.5%
+20 C

Capacity (Ah)
Li DE-INSERTION OUT OF COKE

I = 0.22 (mA/cm²)
EC+DEC+DMC+EMC (3:5:4:1)

-40 °C, 86%

+20 °C
EFFECT OF DISCHARGE RATE ON Li/C CELL AT -40 C

(1) \( I = 0.285 \text{ (mA/cm}^2\) \) @ RT
(2) \( I = 0.00095 \text{ (mA/cm}^2\) \) @ -40 C
(3) \( I = 0.0095 \text{ (mA/cm}^2\) \) @ -40 C
EFFECT OF DISCHARGE RATE ON Li/C CELL AT -40 C

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Potential vs. Li (Volts)

Capacity (Ah)

graphite
Li DIFFUSIVITY IN COKE DETERMINED BY GALVANOSTATIC INTERMITTENT TITRATION TECHNIQUE

![Graph showing diffusivity vs. temperature](image)

- $1.14 \times 10^{-9}$
- $1.38 \times 10^{-10}$
- $6.64 \times 10^{-11}$
- $3.04 \times 10^{-11}$

Temperature (C)

Diffusivity (cm$^2$/sec)
**Electrolyte**

<table>
<thead>
<tr>
<th>LIQUID E'LYTE</th>
<th>SEI</th>
<th>CARBON PARTICLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIFFICULT</td>
<td>Li$^+$</td>
<td>EASY</td>
</tr>
</tbody>
</table>

(a) Li intercalation

\[ [\text{Li}] \]

(b) Li de-intercalation

\[ [\text{Li}] \]

Diffusivity

\[ \text{Diffusivity} \]
CARBON ANODE IS THE SOURCE OF PROBLEM?

<table>
<thead>
<tr>
<th>CARBON ANODE</th>
<th>SEI</th>
<th>LIQUID E'LYTE</th>
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<td>-40 C</td>
<td></td>
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HIGH POLARIZATION AT INTERFACE CAUSED BY:

1. THE SLOW LI DIFFUSION AT -40 C.
2. DIFFUSIVITY CHANGES WITH COMPOSITION.
EFFECT OF PARTICLE SIZE ON LOW TEMPERATURE LI/COKE HALF CELL PERFORMANCE

Charge Capacity (Ah/g)

Cycle Number

-20 C

-30 C

+20 C

- small particle

- large particle

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(1) The EC+DEC+DMC+EMC-based mixed solvent electrolytes is an attractive candidate electrolyte for low temperature applications due to its extended liquidus range.

(2) LiCo(0.2)Ni(0.8)O2 is suitable for low temperature (-40 C) application.

(3) Determined that carbon anodes limit low temperature performance.

(4) Low temperature carbon anode performance is not limited by Li diffusion in the SEI.

(5) Low temperature performance is limited by slow diffusion of Li in the carbon anodes.

(6) To further improve low temperature Li-ion cell performance, the use of alternate anode materials must be investigated.
ACKNOWLEDGMENTS

THE WORK DESCRIBED HERE WAS CARRIED OUT AT JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, UNDER CONTRACT WITH THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION.