Design and fabrication of all-solid-state rechargeable lithium batteries using ceramic electrolytes

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Outline

1. Introduction
   > Why all-solid-state?
   > Tasks in the development of all-solid-state batteries

2. Strategy (cell design)
   > 3D structured solid electrolyte
   > Sol-gel technique to construct a good electrode/electrolyte interface

3. Cell performance
   > All-solid-state rechargeable lithium battery using LLT
   > All-solid-state rechargeable lithium battery using LLZ

4. Conclusions
Extending applications of LIBs

Portable electronic devices → Electric vehicle

Safety
Energy density
Power density

The safety is more important in large-scale batteries.
Electrolyte in LIBs

- **Device**

  - **Anode** (Graphite)
  - **Cathode** (LiCoO$_2$)
  - **Charge**
  - **Discharge**
  - **Inorganic solid electrolyte (non-flammable)**

- **Liquid electrolyte** (flammable organic solvents)

- **Inorganic solid electrolyte** (non-flammable)
Merits of inorganic solid electrolytes

Inorganic solid electrolytes:

- Non-flammability
- Extending the upper limit of operating temperature
- Low self-discharge
- Simple package (bipolar batteries)
- 3D structured battery

-> New battery applications
Current all-solid state batteries

Thin film battery (2D)

2-dimensional (thin-layered) electrode configuration provides high rate performance due to fast lithium ion transport by short distance between cathode and anode, but…

Low capacity!
The electrode material situated away from an electrolyte layer does not work efficiently due to long diffusion length of lithium-ions.

It is difficult to obtain high cell capacity even though thick electrodes are prepared.
## Commercially available thin film batteries

**Solid-State, Rechargeable, Micro-Energy Cells (MECs)**

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>MEC225</th>
<th>MEC220</th>
<th>MEC201</th>
<th>MEC202</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Open Circuit Voltage (OCV)</strong></td>
<td>V</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td><strong>Package Size/Footprint (1)</strong></td>
<td>in. mm</td>
<td>0.5 x 0.5</td>
<td>1.0 x 0.5</td>
<td>1.0 x 1.0</td>
<td>1.0 x 2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.7 x 12.7</td>
<td>25.4 x 12.7</td>
<td>25.4 x 25.4</td>
<td>25.4 x 50.8</td>
</tr>
<tr>
<td><strong>Package Thickness</strong></td>
<td>in. mm</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td><strong>Typical Internal Resistance</strong></td>
<td>Ω</td>
<td>260</td>
<td>120</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td><strong>Maximum Continuous Current</strong></td>
<td>mA</td>
<td>7</td>
<td>15</td>
<td>40</td>
<td>90</td>
</tr>
<tr>
<td><strong>Nominal Capacity Options</strong></td>
<td>mAh</td>
<td>0.13</td>
<td>0.3</td>
<td>0.7</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>1.0</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td><strong>Equivalent Energy in Joules</strong></td>
<td>J</td>
<td>1.8</td>
<td>4</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.5</td>
<td>14</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td><strong>Typical Recharge Time to 90% (at 4.1V CL)</strong></td>
<td>Min.</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td><strong>Operating Temperature Range</strong></td>
<td>°C</td>
<td>-40 to +85</td>
<td>-40 to +85</td>
<td>-40 to +85</td>
<td>-40 to +85</td>
</tr>
<tr>
<td><strong>Operating/Shefl Life</strong></td>
<td>Years</td>
<td>&gt;15</td>
<td>&gt;15</td>
<td>&gt;15</td>
<td>&gt;15</td>
</tr>
<tr>
<td><strong>Recharge Cycles (2)</strong></td>
<td></td>
<td>100,000</td>
<td>100,000</td>
<td>100,000</td>
<td>100,000</td>
</tr>
<tr>
<td><strong>Typical Charge Loss/Year</strong></td>
<td></td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td><strong>Supersede (2)</strong></td>
<td></td>
<td>MEC125</td>
<td>MEC120</td>
<td>MEC101</td>
<td>MEC102</td>
</tr>
</tbody>
</table>

All performance metrics measured at 25°C. See product data sheets for more details.

(1) Does not include connection tabs. Total dimensions of supported tab area is 11.3mm x 2.5mm along one edge of device.
(2) Under typical application usage modes.
(3) MEC200 Series devices require a different PDB pad layout design than MEC100 Series (Not a direct replacement).

Updated 6/26/2012 | DS1016 v.1.6

http://www.cytech.com/products-ips
Interdigitated electrode (3D) configuration

- High cell capacity and high current density
- Reduction of internal resistance by large electrochemical interface per unit volume

This kind of 3D electrode configurations have been suggested by many research groups as a next generation battery structure not only for all-solid-state batteries but also for conventional liquid electrolyte batteries.
3D all-solid-state battery can be prepared by impregnation of cathode and anode materials into the holes on the top and bottom faces of a patterned ceramic electrolyte membrane.
Li⁺-conducting solid electrolytes

<table>
<thead>
<tr>
<th>solid electrolyte</th>
<th>conductivity (S cm⁻¹)</th>
<th>temperature (℃)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₄.2Al₀.2Si₀.8O₄</td>
<td>1.58 × 10⁻³</td>
<td>300</td>
<td>Y. Saito et al. <em>Solid State Ionics.</em> 40/41, 34 (1990)</td>
</tr>
</tbody>
</table>

Lithium lanthanum titanium oxide (LLT) was used to prepare a hole-array structured membrane due to high lithium-ion conductivity and mechanical strength.
Hole array $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$

Perovskite structure

$\sigma = 1.2 \times 10^{-3} \text{ S cm}^{-1} \text{ at R.T.}$

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200 holes on each side
**Powder impregnation**

Active material powder + *ethanol*

Heat treatment

LLT / electrode composite

SEM image

Cross section

Non-contact area

High interfacial resistance !!

Very low capacity

0.025 mA h g⁻¹
Application of precursor sol

LiMn$_2$O$_4$ powder + Li-Mn-O sol

Vacuum impregnation

Heat treatment 700 °C, 10 h

Acetate

Nitrate

Precursor sol works as a binder to provide good contact.
Charge/discharge test

- **Acetate**
  - $E$ / V (vs. Li / Li$^+$)
  - Capacity / mA h g$^{-1}$: 1.3 mA h g$^{-1}$

- **Nitrate**
  - $E$ / V (Li / Li$^+$)
  - Capacity / mA h g$^{-1}$: 42.2 mA h g$^{-1}$

**Without sol:** 0.025 mA h g$^{-1}$

**Components:**
- Cathode: LiMn$_2$O$_4$
- Anode: Li metal
- Electrolyte: Honeycomb LLT/PMMA
- Current: 12.5 μA cm$^{-2}$
- Cut off: 3.0 – 4.3V

**Theoretical capacity:** 148 mA h g$^{-1}$
Formation of 3DOM LLT

Colloidal crystal templating method

3-dimensionally ordered macroporous (3DOM) LLT
3DOM-hybrid hole-array

- Short diffusion length of \( \text{Li}^+ \)
- Large contact area (Low internal resistance)

Simple hole-array

3DOM-hybrid hole-array

Solid electrolyte

Active material

Solid electrolyte
Charge/discharge test

- Cathode: LiMn$_2$O$_4$
- Anode: Li metal
- Electrolyte: porous-layered honeycomb LLT / PMMA
- Current: 12.5 mA cm$^{-2}$
- Cut off: 3.0 – 4.3V

- Hole-array LLT: 42.2 mA h g$^{-1}$
- 3DOM-formed Hole-array LLT: 70.8 mA h g$^{-1}$
Full cell preparation procedure

Li-Mn-O sol + LiMn$_2$O$_4$

Vacuum impregnation  
Calcination  
450 °C, 30 min  
3 times  
Calcination  
450 °C, 2 h  
700 °C, 10 h

Li-Mn-O sol + Li$_4$Mn$_5$O$_{12}$

Vacuum impregnation  
Calcination  
450 °C, 30min  
3 times  
Calcination  
450 °C, 2 h  
600 °C, 10 h

All-ceramic battery
Operation at room temperature

Operation of all-solid-state rechargeable lithium-ion battery at room temperature
**Li₇La₃Zr₂O₁₂**

New solid electrolyte

Li₇La₃Zr₂O₁₂ (LLZ)

**Advantages**

- High lithium-ion conductivity (10⁻⁴ S cm⁻¹ at R.T.)
- High stability against lithium-metal

Can lithium-metal (3861 mA h g⁻¹) be used as anode?

LLT shows the redox reaction of titanium at 1.8 V while LLZ is stable even at 0 V.

=> Lithium-metal can be used as anode in the LLZ system.
**Li metal / LLZ / LiCoO₂ cell**

- **LiCoO₂**
- **LLZ pellet**
- **Li metal**

**230 °C**

**Room temperature**

Scan rate: 1 mV min⁻¹
Cut off: 3.3 – 4.2 V vs. Li / Li⁺

Redox peaks of LiCoO₂ were observed around at 3.9 V vs. Li / Li⁺.
The prepared cell stably worked after a year.

Scan rate : 1 mV min$^{-1}$

Cut off : 3.3 – 4.2 V vs. Li / Li$^+$

As prepared

After a year

Durability test
Bipolar-type battery

- Current collector tab
- Composite of cathode material and solid electrolyte
- Solid electrolyte membrane with hole array structure
- Lithium-metal anode
- Current collector for anode (carbon/nickel composite)
- Honeycomb hole
- Solid-electrolyte substrate
- 3DOM structured solid-electrolyte
- Cathode material

Cell voltage: 200 V
Energy density: > 500 Wh kg\(^{-1}\)
Fast charge/discharge: > 10 min
High safety
Long life
Energy density

Gravimetric energy density / Wh kg⁻¹

Volumetric energy density / Wh L⁻¹

LiCoO₂ (LiNi⁴/₃Mn⁴/₃Co⁴/₃O₂) / graphite

All-solid-state (bipolar-type)

High capacity electrode materials

Lithium-Air

Lithium-Sulfur

Conventional lithium-ion

Nickel-Cadmium

Nickel-Metal Hydride

Lead acid

Energy density
Conclusions

3D electrode configuration is one of prospective ways to improve the performance of all-solid-state rechargeable lithium batteries.

For further improvement of cell performance, the following developments are needed:

• Higher aspect ratio in 3D electrode configuration

• Optimization of electrolyte/electrode interface

• Cell stacking for bipolar-type all-solid-state battery