Lithium Ion Conductive Glass Ceramics: Properties and Application in Lithium Metal Batteries

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Lithium Ion Conductive Glass Ceramics (LICGC\textsuperscript{TM}): Properties and Application in Lithium Metal Batteries

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Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

1) Introduction of OHARA Group

< OHARA INC. >
- Founded: Oct. 1, 1935
- Locations: Chuo-ku, Sagamihara-shi, Kanagawa, Japan
- Total Employee: 430
- Main Products:
  - Optical Glass – Over 200 types of glass line-up in strip, cut disks and pressed blanks
  - Glass Ceramics – Low Thermal Expansion Glass-ceramics (CLEARCERAM®-Z)
  - High Thermal Expansion Glass-ceramics (WMS series)
  - (Over 10 types)
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

1) Introduction of OHARA Group

< OHARA Group Business Domain >

Optical Business Domain
- Pressings, Blocks
- Low Tg Optical Glass
  For Digital Camera, Microscope, Telescope, etc.

Environmental / Energy Business Domain
- Lithium Ion Conductive Glass-ceramics

Electronics Business Domain
- High Homogeneity Glass for i line stepper
- Ultra Low Expansion Glass-ceramics (CLEARCERAM®-Z)
- Synthetic Silica Glass (OHARA Quartz)
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

2) Technologies of OHARA Group

- Glass & Glass-ceramics Composition Engineering Expertise
- Homogeneous Glass production know-how
- Precision Metrology technologies
- Precision Plano – Plano Grinding / Polishing & Cleaning technologies
- Precision Cleaning technologies for Glass substrates
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

2) Technologies of OHARA Group
   - Glass-ceramics Technology

- Composition / Structure: Nono-scale aggregates of poly-crystalline particles are dispersed among amorphous glass matrix

- Benefits: Added properties (values) to the original glass, with Improved Mechanical Strength and Processability
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature

- Glass-ceramics, to have isotropically dispersed Lithium-Ion Conductive Crystal particles and an amorphous glass phase

- Ohara has a US trademark on LICGC™

- Features
  -> Top level Ionic Conductivity among Inorganic Materials (In the order of $10^{-4}$ S/cm at RT)
  -> Thermally Stable up to 600 °C, Nonflammable.
  -> Can be Handled in Air.
  -> No Through Hole (No H₂O Penetration)
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature

Presently the supply of LICGC™ is basically concentrated in membrane form. 2 different materials from different processes:

a.) AG-01 melted & polished plates
- \( \text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2 \)
- Conductivity: \( \sim \) 1 \times 10^{-4} \text{ S/cm at 25 °C} 
- Proved seawater stability (>2 years*)
  *Evidenced by past evaluations at Polyplus Battery company.

b.) LICGC™ Tape Cast & Sintered plates (Under Development)
- \( \text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2 \)
- Conductivity: \( \sim \) 3 \times 10^{-4} \text{ S/cm at 25 °C} 
- Scalable in terms of size & quantity

< Typical Membranes Sizes >
- Sq.1” x 150 um thick, Dia.2” x 250 um thick, Sq.2” x 200 um thick
- ~ Up to 6” Dia. is possible
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature (Where does LICGC positions in Lithium-Ion Conductive Inorganic Materials?)

LICGC™ (Original Powder Material)

LICGC™ (AG-01 Membrane)
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature

Thermally Stable up to 600 °C

Nonflammable, Can be Handled in Air.

- No Weight Change is detected at heating to 600 °C.
- No Exothermal Reaction is detected at heating to 600 °C.
- Measured up to 600 °C in Air.
Blocking moisture penetration
(Moisture Permeability Measurement)

Moisture permeability (g m\(^{-2}\) day\(^{-1}\))

Time (hour)

Mocon Permatran 3/33
### 3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
#### 3-ii) General Properties (AG-01)

<table>
<thead>
<tr>
<th>Chemical Properties</th>
<th>Water Resistance in Powder form (RW(P) in JOGIS Class)</th>
<th>Class 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid Resistance in Powder form (RW(P) in JOGIS Class)</td>
<td>Class 1</td>
</tr>
<tr>
<td><strong>Mechanical Properties</strong></td>
<td>4 Point Bending Strength</td>
<td>140N/mm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Knoop Hardness (Hk)</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>Specific Gravity</td>
<td>3.05</td>
</tr>
<tr>
<td><strong>Thermal Properties</strong></td>
<td>Coefficient of Thermal Expansion</td>
<td>94 x 10&lt;sup&gt;-7&lt;/sup&gt;/degree C (30 ~ 350degree C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>82 x 10&lt;sup&gt;-7&lt;/sup&gt;/degree C (350 ~ 600degree C)</td>
</tr>
</tbody>
</table>
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-iii) Composition & Structure (AG-01)

Main Crystal Phase: $\text{Li}_{1+x} \text{Al}_x \text{Ge}_y \text{Ti}_{2-x-y} \text{P}_3 \text{O}_{12}$
(NASICON type crystals)

Sub Crystal Phase: $\text{Li}_{1+x+3z} \text{Al}_x (\text{Ge,Ti})_{2-x} (\text{Si}_2 \text{PO}_4)_3$
(NASICON type crystals)

Sub Crystal Phase: $\text{AlPO}_4$

$\text{Li}_{1+x+3z} \text{Al}_x (\text{Ti,Ge})_{2-x} \text{Si}_{3z} \text{P}_{3-z} \text{O}_{12}$
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-iii) Composition & Structure (AG-01)

- X-Ray Diffraction

![X-Ray Diffraction Pattern]

- **LiTi₂P₃O₁₂**
- **AlPO₄**
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-iii) Composition & Structure (AG-01)
   - TEM & EDX

\[ \text{Li}_{1+x} \text{Al}_x \text{Ge}_y \text{Ti}_{2-x-y} \text{P}_3 \text{O}_{12} \]  
\[ \text{AlPO}_4 \]  
\[ \text{Li}_{1+x+3z} \text{Al}_x (\text{Ge,Ti})_{2-x} (\text{Si}_z \text{PO}_4)_3 \]
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-iii) Composition & Structure (AG-01)

- Microstructure & Compositional distribution Observations
  by Low Acceleration Scanning Microscope for the cross-section of LICGC plate

![Secondary Electron Imaging (SEI, x20K)](image1)
![Backscattered Electron Imaging (BEI, x20K)](image2)

Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12} (Light Grey Back Ground)
Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}SizPO_4_3 (White Spot)
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-iii) Composition & Structure (AG-01)

- Li Ion Conduction Mechanism in the material: Vacancy Diffusion

PO₄
(Ti,Ge)O₆
Li(filled)
Li(vacancy)

C-axis
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-iii) Composition & Structure

Complex Impedance plot for LICGC™ (Original Powder Material)

Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-iv) Manufacturing Process (AG-01)

Mixing Raw Materials ($\text{Li}_2\text{CO}_3$, $\text{Al(PO}_3\text{)}_3$, $\text{SiO}_2$, $\text{H}_3\text{PO}_4$, $\text{TiO}_2$, $\text{GeO}_2$)

Melting

Glass Drawing & Forming

Crystallization

Mechanical Processing

Lithium-Ion Conductive Glass-ceramics

*Efficient mfg Process (Tape Cast & Sintered Plating) is now under development. The process realize a near-net shape and yields lesser removal.
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-v) Application
(Solid Electrolyte for Elemental Li / Air Battery)

Li / Air Cell Structure

Reaction of Lithium-Air Battery
- Cathode: \( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{(OH)}^- \)
- Anode: \( 4\text{Li} \rightarrow 4\text{Li}^{+} + 4e^- \)
- Cell: \( 4\text{Li} + \text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow 4\text{LiOH} \)
3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-v) Applications (Solid Electrolyte for Elemental Li / Air Battery)

Li / Air Cell Performance
Discharge curve for the Demonstrative Primary Li / Air Cell

- Discharge current: 0.3mA/cm²
- Temperature: 25°C
- Discharge ended with over 95% designed capacity
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-v) Applications (Solid Electrolyte for Elemental Li / Air Battery)

Li / Air Cell Performance

Charge-Discharge Curve for the Demonstrative Secondary Li/Air Cell

Charge-discharge current: 0.1-1.0mA/cm²
Temperature: 25°C
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-v) Applications (Solid Electrolyte for Elemental Li / Seawater Battery)

Li / Seawater Cell Structure

**Reaction of Lithium-Water Battery**
- Cathode: $2H_2O \rightarrow 2(OH)^- + H_2$
- Anode: $2Li \rightarrow Li^{+} + e^-$
- Cell: $2Li + 2H_2O \rightarrow 2LiOH + H_2$
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)
3-v) Applications (Solid Electrolyte for Elemental Li / Seawater Battery)

Water / Seawater Resistivity of LICGC™ AG-01 in Static test.

![Graph showing Ionic conductivity vs Storage time]

- Pure water (40 °C)
- Synthetic seawater (RT)
Lithium Ion Conductive Glass Ceramics (LICGC\textsuperscript{TM}):
Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC\textsuperscript{TM})
3-v) Applications (Solid Electrolyte for Elemental Li / Seawater Battery)

**Li / Seawater Cell Performance**

Discharge curve for the Demonstrative Primary Li/Seawater Cell

![Discharge curve](image)

- Discharge current: 0.1mA/cm\textsuperscript{2}
- Temperature: 25°C
- (Li anode capacity: 129 mAh)
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

4) Conclusion

- The OHARA Group has developed Lithium Ion Conductive Glass Ceramics (LICGC™) materials, utilizing our own technology, which are water impermeable and non-flammable.

- The LICGC™ materials embody unique properties and characteristics and are suitable to be used as Solid Electrolytes for Elemental Lithium Batteries. LICGC™ serves to protect the Li anode from oxidation by water or other oxidants from outside of the cell.

- We have verified the performance of the LICGC™ materials as Solid Electrolytes in prototype cell testing in Elemental Li Batteries (Li/Air and Li/Seawater).

- The OHARA Group believes the LICGC™ materials will contribute to the advancement of higher capacity, more innovative energy storage beyond present Lithium Ion Batteries.
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

5) Acknowledgement

“We would like to acknowledge and thank PolyPlus Battery Company for their technical contributions in the area of Elemental Lithium / Air, Lithium / Seawater battery development work.”
End of the Presentation.
Thank you for your listening.