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

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   3-iv) Manufacturing Process
   3-v) Application
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5) Acknowledgement
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)
2) Technologies of OHARA Group

- Glass & Glass-ceramics Composition Engineering Expertise
- Homogeneous Glass production know-how
- Precision Metrology technologies
- Precision Plano – Plano Grindng / 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
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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 LIC-GC™ is basically concentrated in membrane form. 2 different materials from different processes:

a.) AG-01 melted & polished plates
- Li₂O-Al₂O₃-SiO₂-P₂O₅-TiO₂-GeO₂
- Conductivity : ~ 1 x 10⁻⁴ 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)
- Li₂O-Al₂O₃-SiO₂-P₂O₅-TiO₂
- Conductivity : ~ 3 x 10⁻⁴ 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 LIC-GC positions in Lithium-Ion Conductive Inorganic Materials?)

![Graph showing the position of LIC-GC in the context of other lithium-ion conductive inorganic materials.](image_url)
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-i) Main Feature

**Thermally Stable up to 600 °C**

<table>
<thead>
<tr>
<th>Thermogravimetry</th>
<th>DTA /µV/mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG /%</td>
<td>exo</td>
</tr>
</tbody>
</table>

- **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**

**Differential Thermal Analysis**

**Nonflammable, Can be Handled in Air.**

**Stable against Flame**

**Stable in Water**

Thermally Stable up to 600 °C

Nonflammable, Can be Handled in Air.
3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature

Blocking moisture penetration
(Moisture Permeability Measurement)
## 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>Acid Resistance in Powder form (RW(P) in JOGIS Class)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1</td>
<td>Class 1</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>4 Point Bending Strength</th>
<th>140N/mm²</th>
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<tbody>
<tr>
<td></td>
<td>Knoop Hardness (Hk)</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>Specific Gravity</td>
<td>3.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Properties</th>
<th>Coefficient of Thermal Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>94 x 10⁻⁷/degree C (30 ~ 350degree C)</td>
</tr>
<tr>
<td></td>
<td>82 x 10⁻⁷/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: $\text{Li}_{1+x+3z} \text{Al}_x \text{Ge}_y \text{Ti}_{2-x-y} \text{Si}_3z \text{P}_{3-z} \text{O}_{12}$
(NASICON type crystals)

Sub Crystal Phase: $\text{AlPO}_4$
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](image)

- Intensity (counts) vs. 2θ (Cu Kα)
- Peaks for LiTi₂P₃O₁₂ and 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

\[ \text{Li}_{1+x} \text{Al}_x \text{Ge}_y \text{Ti}_{2-x-y} \text{P}_3 \text{O}_{12} \]

\[ \text{AlPO}_4 \]

\[ \text{Li}_{1+x+3z} \text{Al}_x (\text{Ge}, \text{Ti})_{2-x} (\text{Si}_z \text{PO}_4)_3 \]
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

\[ \text{Li}_{1+x}^{1+3z} \text{Al}_x \text{Ge}_y \text{Ti}_{2-x-y} \text{P}_3 \text{O}_{12} \] (Light Grey Back Ground)

\[ \text{Li}_{1+x}^{1+3z} \text{Al}_x (\text{Ge, Ti})_{2-x-y} (\text{Si}_2 \text{PO}_4)_3 \] (White Spot)

AlPO₄ (Dark Grey 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
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 ($Li_2CO_3$, $Al(PO_3)_3$, $SiO_2$, $H_3PO_4$, $TiO_2$, $GeO_2$)

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 realizes 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: $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$
Anode: $4Li \rightarrow 4Li^++4e^-$
Cell: $4Li + O_2 + 2H_2O \leftrightarrow 4LiOH$

Energy Density Comparison

<table>
<thead>
<tr>
<th>Battery Type</th>
<th>Wh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-MH</td>
<td>100</td>
</tr>
<tr>
<td>LIB</td>
<td>200</td>
</tr>
<tr>
<td>Zn-Air</td>
<td>300</td>
</tr>
<tr>
<td>Li-Air</td>
<td>600</td>
</tr>
</tbody>
</table>

Li / Air Prototype Cell for solid electrolyte evaluation (Using Sq.2” LIC-GC™ AG-01)
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**

Discharge curve for the Demonstrative Primary Li / Air Cell

![Discharge curve](image)

- **Discharge current**: 0.3mA/cm²
- **Temperature**: 25°C
- **Discharge ended with over 95% designed capacity**
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

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

Li / Seawater Prototype Cell
for solid electrolyte evaluation
(Using Sq.1” LICGC™ AG-01)

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.*
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 Performance
Discharge curve for the Demonstrative Primary Li/Seawater Cell

Discharge current: 0.1mA/cm²
Temperature: 25°C

(Li anode capacity: 129 mAh)
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.
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.