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

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   3-iv) Manufacturing Process
   3-v) Application
4) Conclusion
5) Acknowledgement
Lithium Ion Conductive Glass Ceramics (LIC-GC®): 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 – HDD Substrate Blanks (TS-10®)
  Low Thermal Expansion Glass-ceramics (CLEARCERAM®-Z)
  High Thermal Expansion Glass-ceramics (WMS series)
  (Over 10 types)
Lithium Ion Conductive Glass Ceramics (LIC-GC®): 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
- Glass-ceramics for HD (TS-10®)
- 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 Grinding / Polishing & Cleaning technologies
- Precision Cleaning technologies for Glass substrates
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.

Silica Glass

OHARA Ultra Low Expansion Glass (CLEARCERAM®-Z)

2mm
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 LIC-GC®

- 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)

![The Arrhenius plot on LIC-GC® (Original Powder Material)](image)
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

b.) LIC-GC® 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: \( \sim 3 \times 10^{-4} \text{ S/cm at } 25^\circ \text{C} \)
- 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 (LIC-GC®)
Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

[Graph showing the conductivity of various lithium ion conductive materials at different temperatures.]

LIC-GC® (Original Powder Material)

LIC-GC® (AG-01 Membrane)
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

3-i) Main Feature

**Thermally Stable up to 600 °C**

Thermogravimetry

- No Weight Change is detected at heating to 600 °C.

Differential Thermal Analysis

- No Exothermal Reaction is detected at heating to 600 °C.

Measured up to 600 °C in Air

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

Stable against Flame

Stable in Water
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

3-i) Main Feature

Blocking moisture penetration
(Moisture Permeability Measurement)

[Graph showing moisture permeability over time]

Mocon Permatran 3/33
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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>
<tr>
<td>Mechanical Properties</td>
<td>4 Point Bending Strength</td>
<td>140N/mm²</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>Thermal Properties</td>
<td>Coefficient of Thermal Expansion</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>94 x 10⁻⁷/degree C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(30 ~ 350degree C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>82 x 10⁻⁷/degree C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(350 ~ 600degree C)</td>
</tr>
</tbody>
</table>
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

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

\( \text{Li}_{1+x+3z} \text{Al}_x (\text{Ti, Ge})_{2-x} \text{Si}_3z \text{P}_{3-z} \text{O}_{12} \)
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

- X-Ray Diffraction
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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 (LIC-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

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

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

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

**Li$_{1+x}$Al$_x$Ge$_y$Ti$_{2-x-y}$P$_3$O$_{12}$**
(Light Grey Back Ground)

**Li$_{1+x+3z}$Al$_x$(Ge,Ti)$_{2-x}$(Si$_z$PO$_{4}$)$_3$**
(White Spot)
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

- Li Ion Conduction Mechanism in the material: Vacancy Diffusion

\[ \text{Li}^{\text{filled}} \quad \text{Li}^{\text{vacancy}} \quad (\text{Ti, Ge})_6\text{O}_{12} \quad \text{PO}_4 \]
Lithium Ion Conductive Glass Ceramics (LIC-GC®):
Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)
3-iii) Composition & Structure

Complex Impedance plot for LIC-GC® (Original Powder Material)

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

3-iv) Manufacturing Process (AG-01)

Mixing Raw Materials (Li₂CO₃, Al(PO₃)₃, SiO₂, H₃PO₄, TiO₂, GeO₂)

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 (LIC-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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>Energy Density (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>500</td>
</tr>
</tbody>
</table>

(OHARA Lithium-Ion Conducting Glass-ceramics (AG-01))
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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 (LIG-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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 Curve](image)

**Li / Air Cell Performance**

- **Charge-discharge current:** 0.1-1.0mA/cm²
- **Temperature:** 25°C

**Cell Voltage vs. Time (hour)**

- **Cell voltage (mV):** 0, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000
- **Time (hour):** 0, 10, 20, 30, 40, 50, 60
- **Current (mA/cm²):** 0.1, 0.3, 0.5, 1.0
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

**Li / Seawater Cell Structure**

- Cathode (Pt- catalysis)
- Aqueous Solution
- OHARA Lithium-Ion Conducting Glass-ceramics (AG-01)
- Anode Protection film
- Anode (Lithium)

**Reaction of Lithium-Water Battery**

Cathode: \(2H_2O \rightarrow 2(OH)^- + H_2\)

Anode: \(2Li \rightarrow Li++e^-\)

Cell: \(2Li + 2H_2O \rightarrow 2LiOH + H_2\)

Li / Seawater Prototype Cell for solid electrolyte evaluation

(Using Sq.1’’ LIC-GC® AG-01)
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

Water / Seawater Resistivity of LIC-GC® AG-01 in Static test.
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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 (LIC-GC®) materials, utilizing our own technology, which are water impermeable and non-flammable.

- The LIC-GC® materials embody unique properties and characteristics and are suitable to be used as Solid Electrolytes for Elemental Lithium Batteries. LIC-GC® 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 LIC-GC® materials as Solid Electrolytes in prototype cell testing in Elemental Li Batteries (Li/Air and Li/Seawater).

- The OHARA Group believes the LIC-GC® 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.