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

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

The Lithium Ion Conductive Glass Ceramics (EQ-CGCS)

i) Main Feature
ii) General Properties
iii) Composition & Structure
iv) Manufacturing Process
- Glass & Glass-ceramics Compositional Engineering Expertise
- Homogeneous Glass production know-how
- Precision Metrology technologies
- Precision Plano – Plano Grinding / Polishing & Cleaning technologies
- Precision Cleaning technologies for Glass substrates
- **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
- Glass-ceramics, to have isotropically dispersed Lithium-Ion Conductive Crystal particles and an amorphous glass phase

- 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 $H_2O$ Penetration)
Presently the supply of EQ-CGCS is basically concentrated in membrane form.

**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*)**

Membrane in Dia.2”x250um thickness
**Main Feature (Where does EQ-CGCS positions in Lithium-Ion Conductive Inorganic Materials?)**

- **LISICON** (Li$_{14}$ZnGe$_4$O$_{16}$)
- Li$_2$O $\cdot$ 11Al$_2$O$_3$ (Line Data)
- Li$_{2}$S-P$_2$S$_5$ (Point Data)
- Li$_{3.5}$V$_{0.5}$Ge$_{0.5}$O$_4$
- Li$_{2}$Ti$_3$O$_7$
- Li$_3$N
- Li$_{1.5}$Al$_{0.3}$Ti$_{1.7}$P$_3$O$_{12}$

**Graph Details**

- Log $\sigma$ (Scm$^{-1}$)
- $1000/T$ (K$^{-1}$)
- Temperature range: 13$^\circ$C to 727$^\circ$C

(Original Powder Material)

(Membrane)
Thermally Stable up to 600°C

Thermogravimetry
TG /%

Differential Thermal Analysis
DTA /(uV/mg)

↑ exo

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

No Exothermic 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
Blocking moisture penetration
(Moisture Permeability Measurement)

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### ii) General Properties

<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>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>94 x 10⁻⁷/degree C (30 ~ 350degree C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>82 x 10⁻⁷/degree C (350 ~ 600degree C)</td>
</tr>
</tbody>
</table>
iii) Composition & Structure

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

Sub Crystal Phase: \( \text{AlPO}_4 \)
iii) Composition & Structure

- X-Ray Diffraction

![X-Ray Diffraction Pattern]

In the figure, the peaks labeled (113), (014), (024), (202), (211), (116), (300), (223), (312), (134), (042), (2110), (410), (2110), (410), (220), (312), (134), (042), (137), (0012) correspond to the crystallographic planes of LiTi$_2$P$_3$O$_{12}$ and AlPO$_4$. The peaks are used for the identification and analysis of the crystal structure.
iii) Composition & Structure

- TEM & EDX

\[ \text{Li}_{1+x+3z}\text{Al}_x\text{Ge}_y\text{Ti}_{2-x-y}\text{P}_3\text{O}_{12} \]

\[ \text{AlPO}_4 \]

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

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

- *AlPO*$_4$ (Dark Grey Spot)

- Secondary Electron Imaging (SEI, x20K)

- Backscattered Electron Imaging (BEI, x20K)

- 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$_{2}$PO$_4$$_3$ (White Spot)
iii) Composition & Structure

- Li Ion Conduction Mechanism in the material: Vacancy Diffusion
iii) Composition & Structure

Complex Impedance plot for EQ-CGCS® (Original Powder Material)

Rb: Attributed to “Grain Boundary”

Rg: Attributed to “Bulk of Grain”
iv) Manufacturing Process

*Efficient mfg Process (Tape Cast & Sintered Plating) is now under development. The process realize a near-net shape and yields lesser removal.