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

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4) Conclusion
5) Acknowledgement

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

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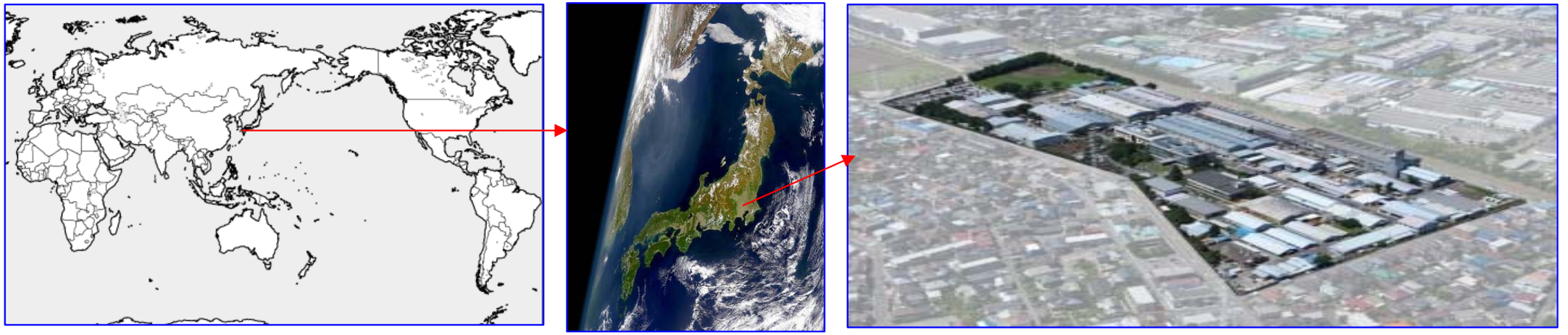
## 1) Introduction of OHARA Group

< 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

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## 1) Introduction of OHARA Group

< OHARA Group Business Domain >

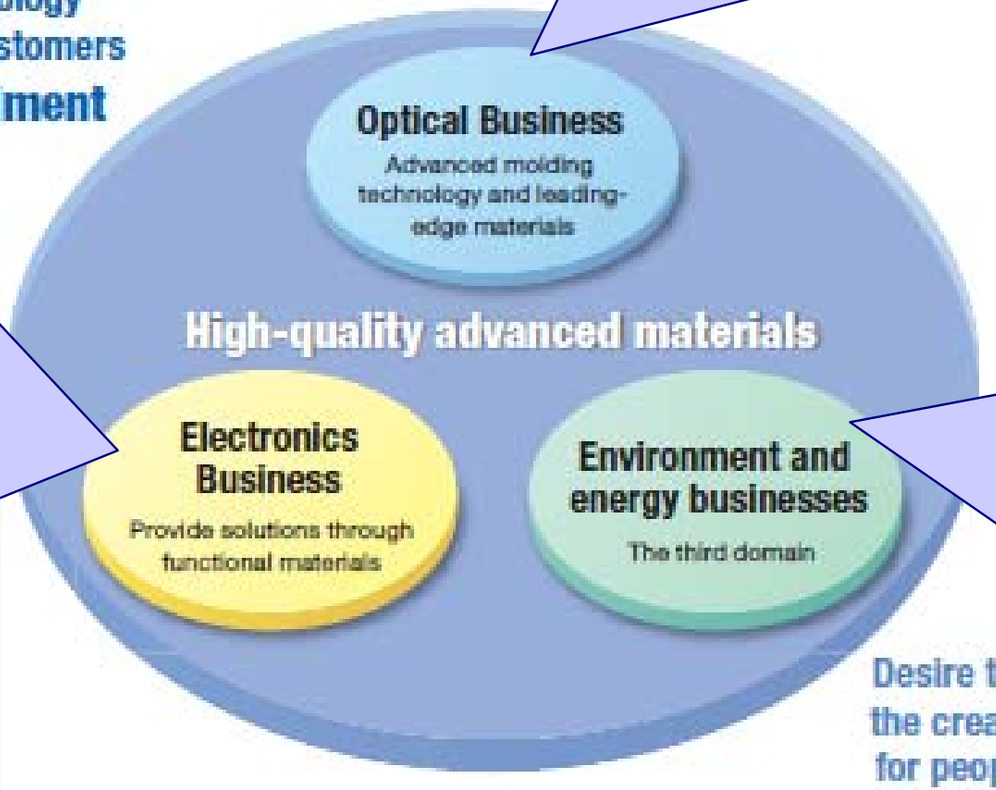
### Optical Business Domain

- Pressings, Blocks
- Low Tg Optical Glass

For Digital Camera, Microscope, Telescope, etc.

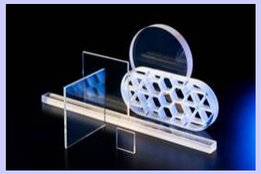
Innovating Technology Together with Customers

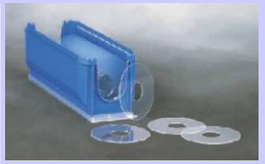
"Dream Fulfillment Company"




### Electronics Business Domain

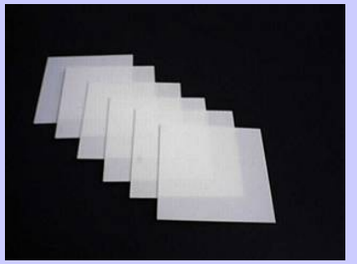
- High Homogeneity Glass for i line stepper
- Glass-ceramics for HD (TS-10®)
- Ultra Low Expansion Glass-ceramics (CLEARCERAM®-Z)
- Synthetic Silica Glass (OHARA Quartz)





### Environmental / Energy Business Domain

- Lithium Ion Conductive Glass-ceramics



Desire to contribute to the creating the future for people and society

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

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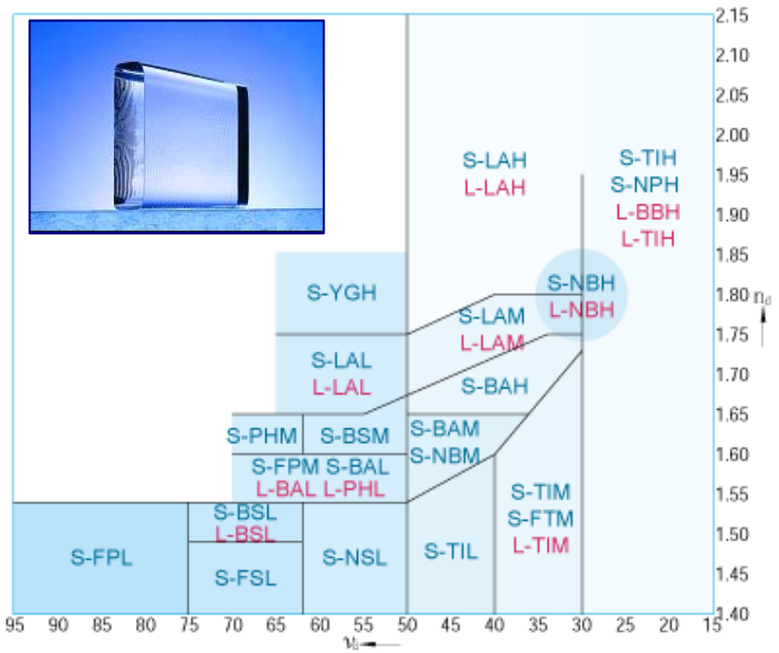
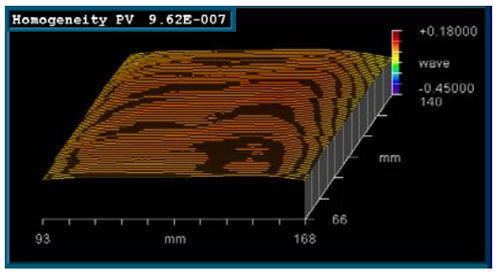
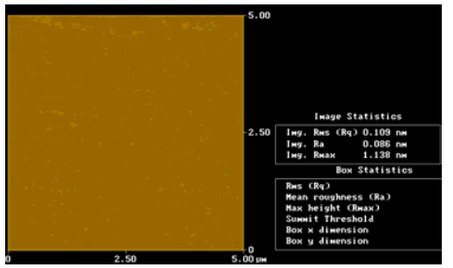
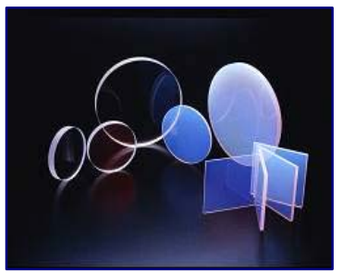
## 2) Technologies of OHARA Group

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

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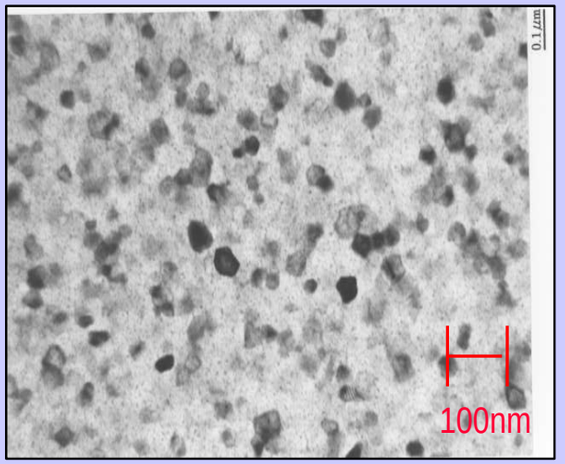
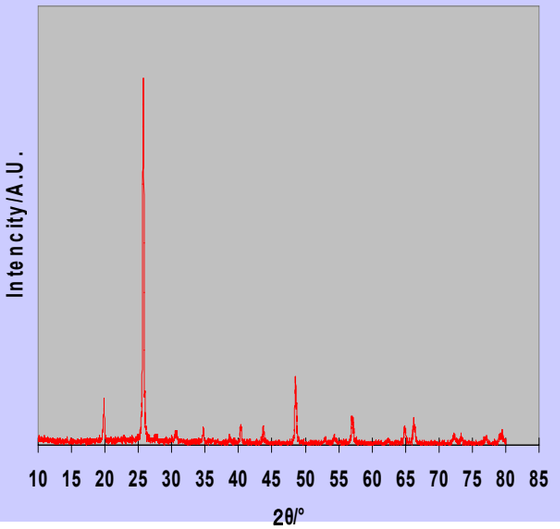
## 2) Technologies of OHARA Group

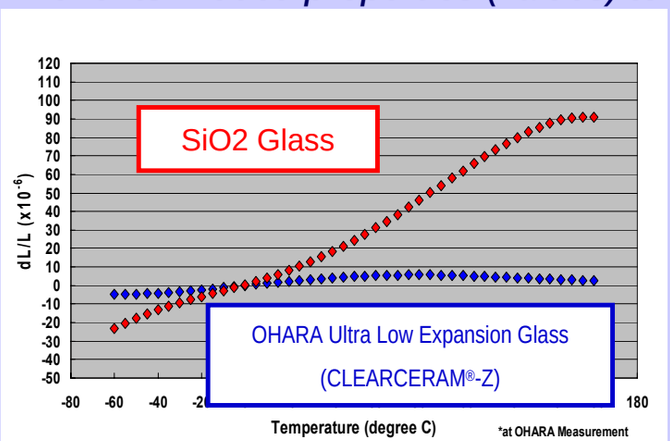
### - Glass-ceramics Technology

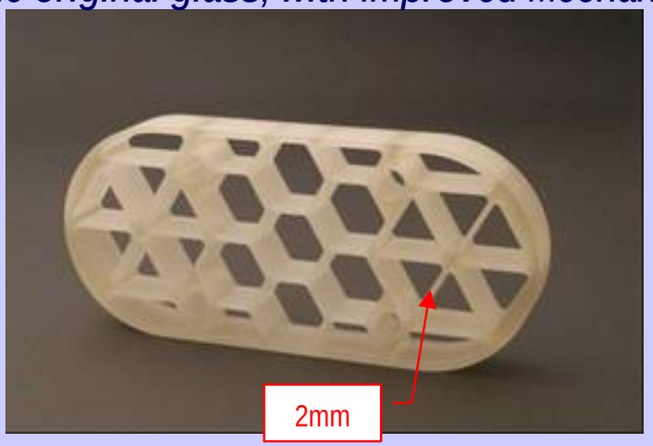
- Composition / Structure: Nono-scale aggregates of poly-crystalline particles are dispersed among amorphous glass matrix

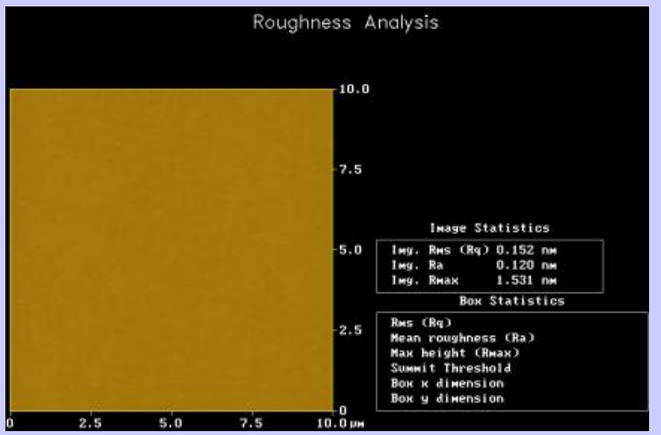



- Benefits: Added properties (values) to the original glass, with Improved Mechanical Strength and Processability



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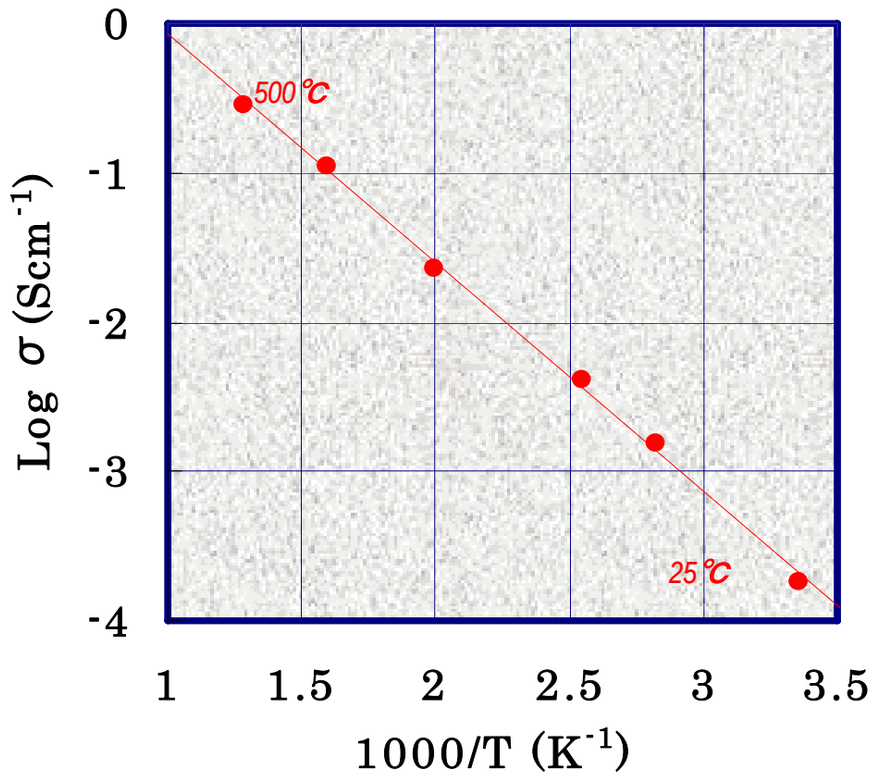
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

### 3-i) Main Feature

- Glass-ceramics, to have isotropically dispersed Lithium-Ion Conductive Crystal particles and an amorphous glass phase
  (OHARA unique technologies, Patent Applied and Registered in JP, US and EU)

- 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 ℃, Nonflammable.
  -> Can be Handled in Air.
  -> No Through Hole (No $H_2O$ Penetration)




The Arrhenius plot on LIC-GC®
(Original Powder Material)

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

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## 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*

- $Li_2O$-$Al_2O_3$-$SiO_2$-$P_2O_5$-$TiO_2$-$GeO_2$
- Conductivity : ~ 1 x $10^{-4}$ S/cm at 25 ° C
- Proved seawater stability (>2 years*)

**Evidenced by past evaluations at Polyplus Battery company.*

*b.) LIC-GC® Tape Cast & Sintered plates (Under Development)*

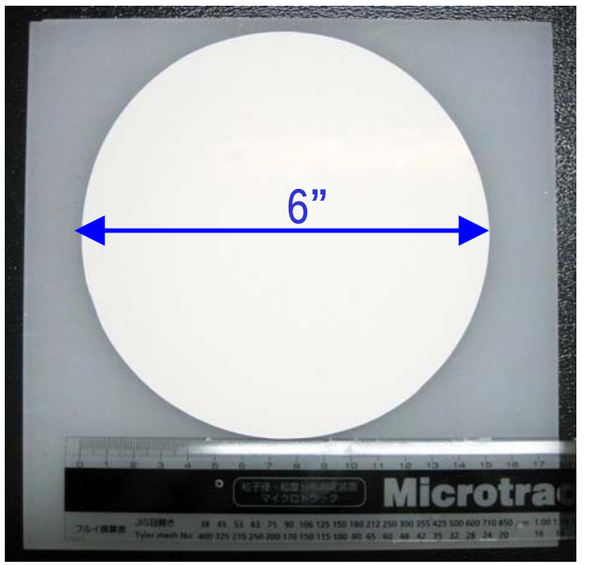
- $Li_2O$-$Al_2O_3$-$SiO_2$-$P_2O_5$-$TiO_2$
- Conductivity : ~ 3 x $10^{-4}$ S/cm at 25 ° C
- Scalable in terms of size & quantity

< 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

AG-01 Membrane
in Dia.2"x250um thickness




LIC-GC® Tape Cast & Sintered Plate
Membrane in Dia.6"x250um thickness

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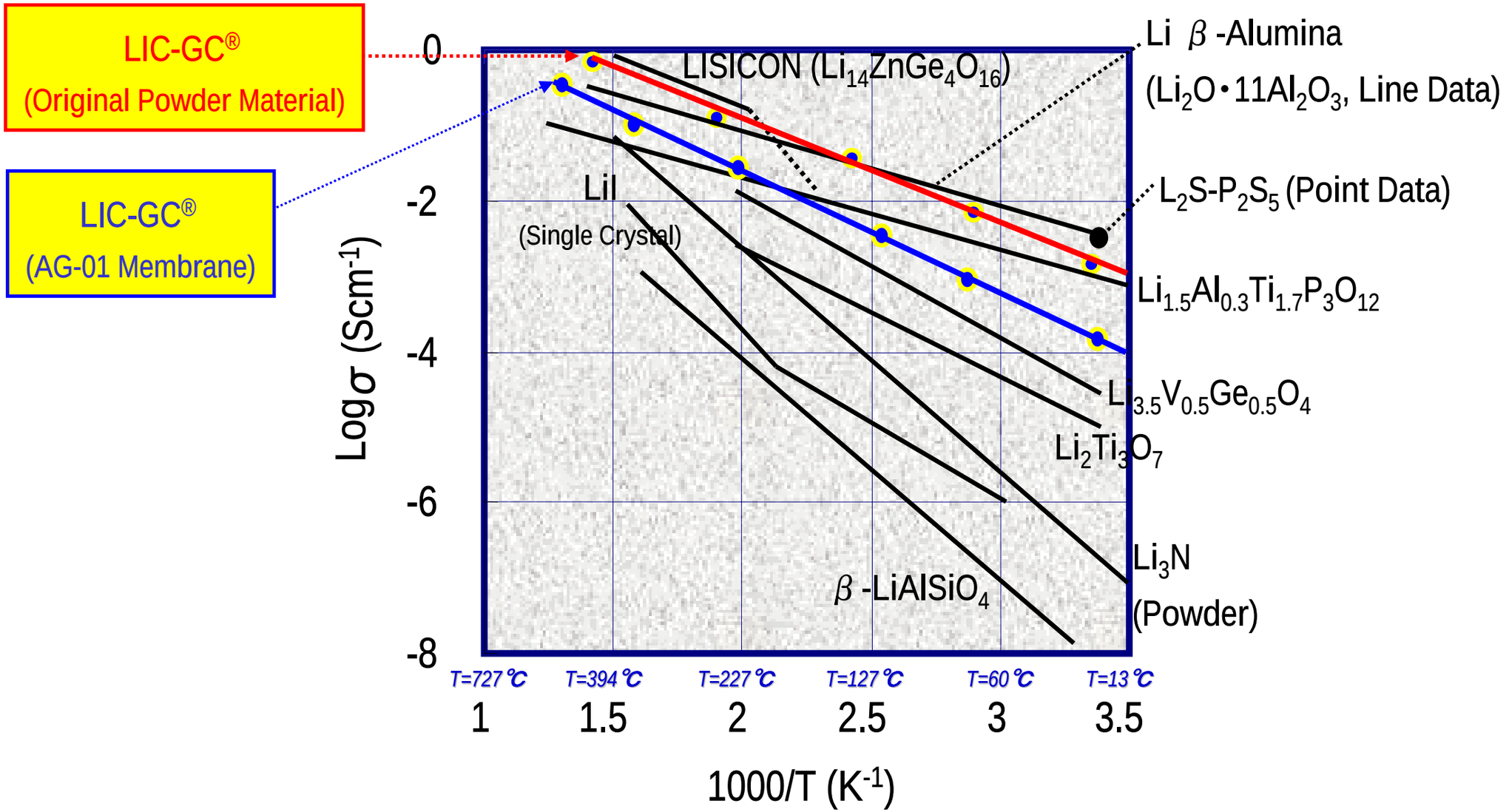
## *3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)*

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



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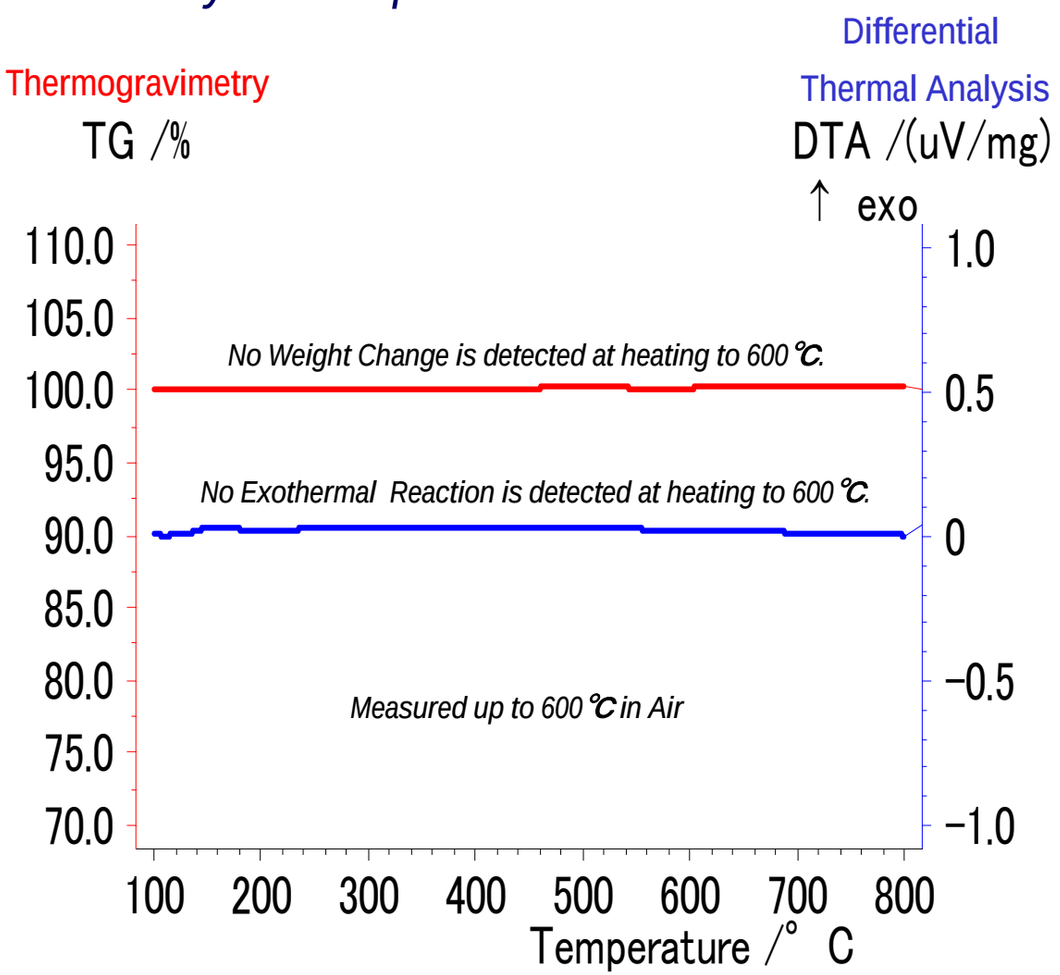
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

### 3-i) Main Feature

*Thermally Stable up to 600℃*




*Nonflammable, Can be Handled in Air.*

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

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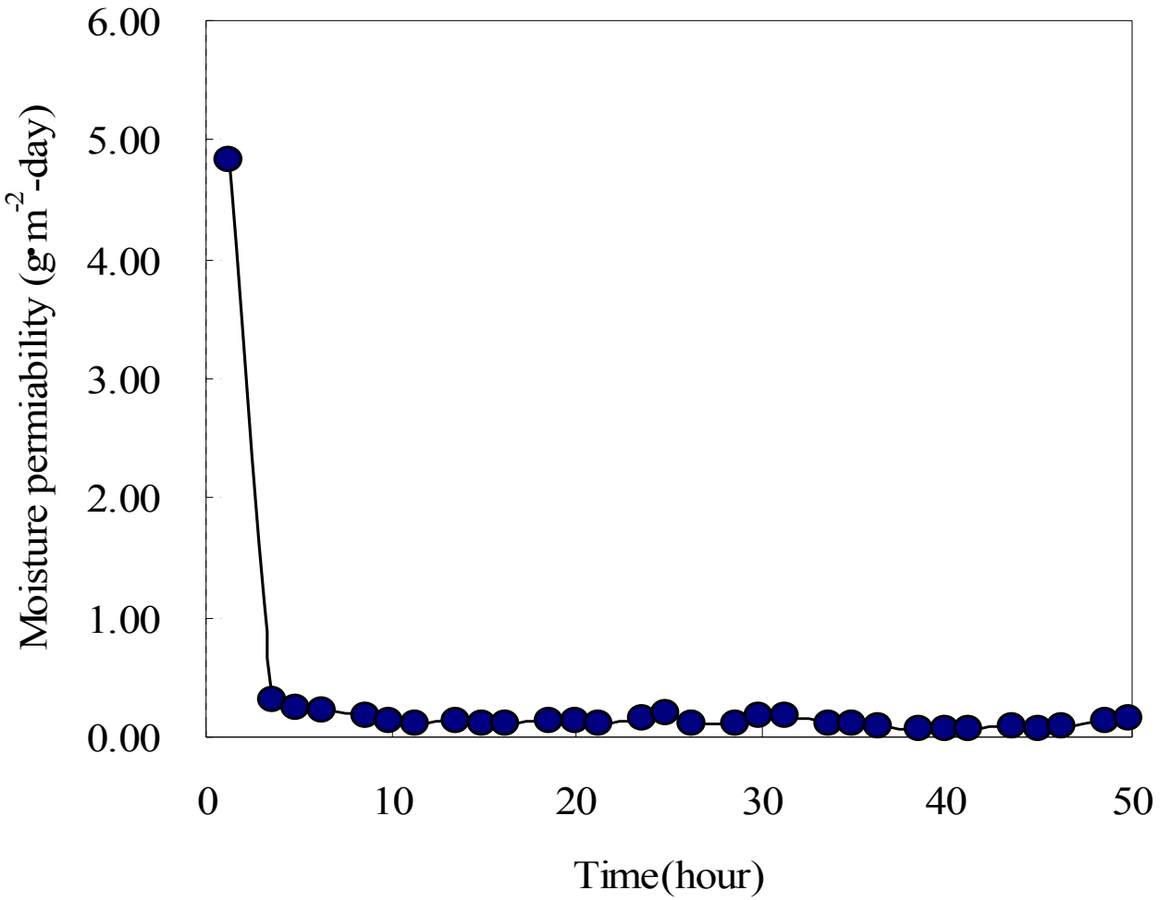
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

### 3-i) Main Feature

*Blocking moisture penetration*
*(Moisture Permeability Measurement)*



Mocon Permatran 3/33

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

### 3-ii) General Properties (AG-01)

| | | |
|---|---|---|
| Chemical Properties | Water Resistance in Powder form (RW(P) in JOGIS Class) | Class 1 |
| | Acid Resistance in Powder form (RW(P) in JOGIS Class) | Class 1 |
| Mechanical Properties | 4 Point Bending Strength | $140 N/mm^2$ |
| | Knoop Hardness (Hk) | 590 |
| | Specific Gravity | 3.05 |
| Thermal Properties | Coefficient of Thermal Expansion | $94 \times 10^{-7}$/degree C (30 ~ 350degree C) |
| | | $82 \times 10^{-7}$/degree C (350 ~ 600degree C) |

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

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

Main Crystal Phase: $Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12}$
(NASICON type crystals)

Sub Crystal Phase: $Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3$
(NASICON type crystals)

$$\left.\begin{array}{l} \text{Main Crystal Phase: } Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12} \\ \qquad\qquad\qquad\qquad \text{(NASICON type crystals)} \\ \\ \text{Sub Crystal Phase: } Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3 \\ \qquad\qquad\qquad\qquad \text{(NASICON type crystals)} \end{array}\right\} Li_{1+x+3z}Al_x(Ti,Ge)_{2-x}Si_{3z}P_{3-z}O_{12}$$

Sub Crystal Phase: $AlPO_4$

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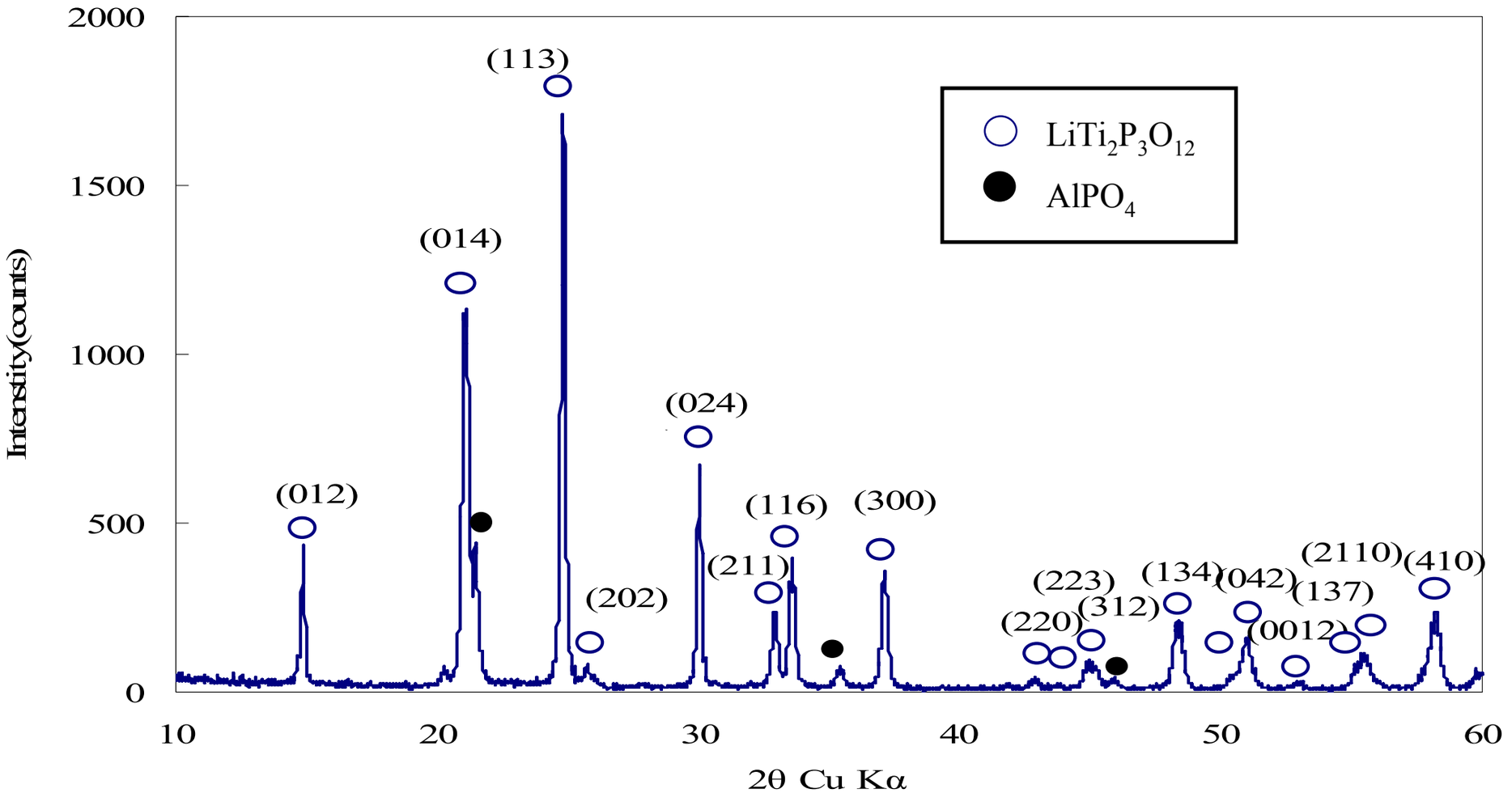
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

- X-Ray Diffraction



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

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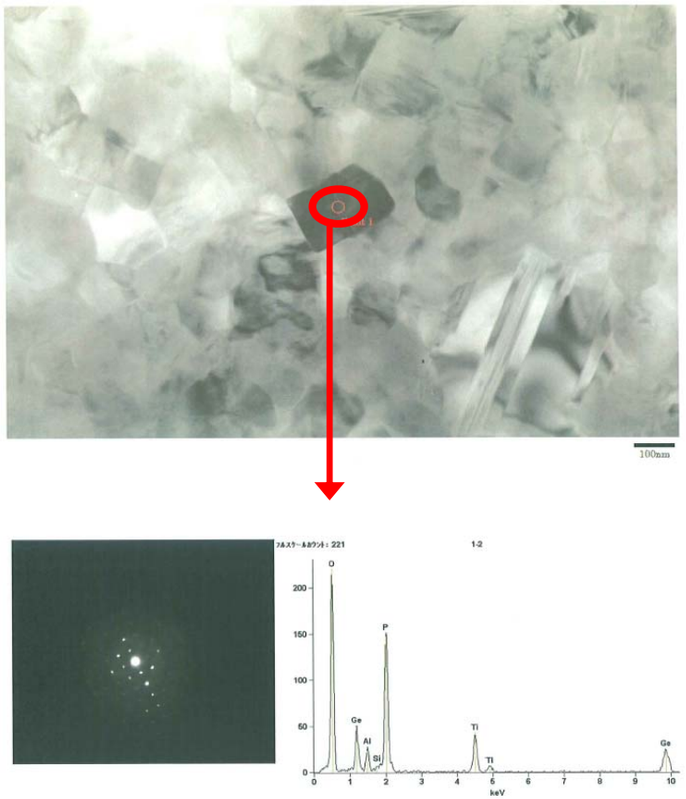
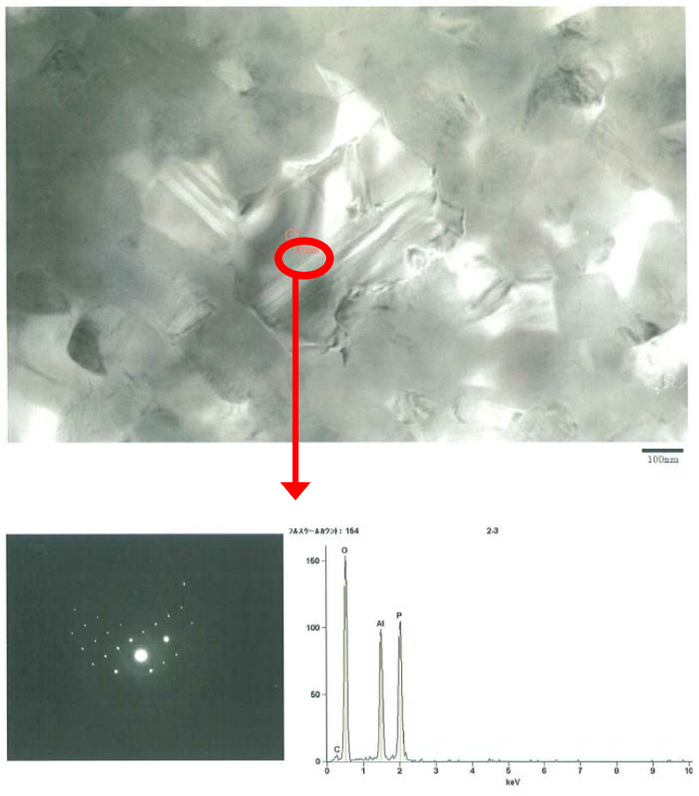
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

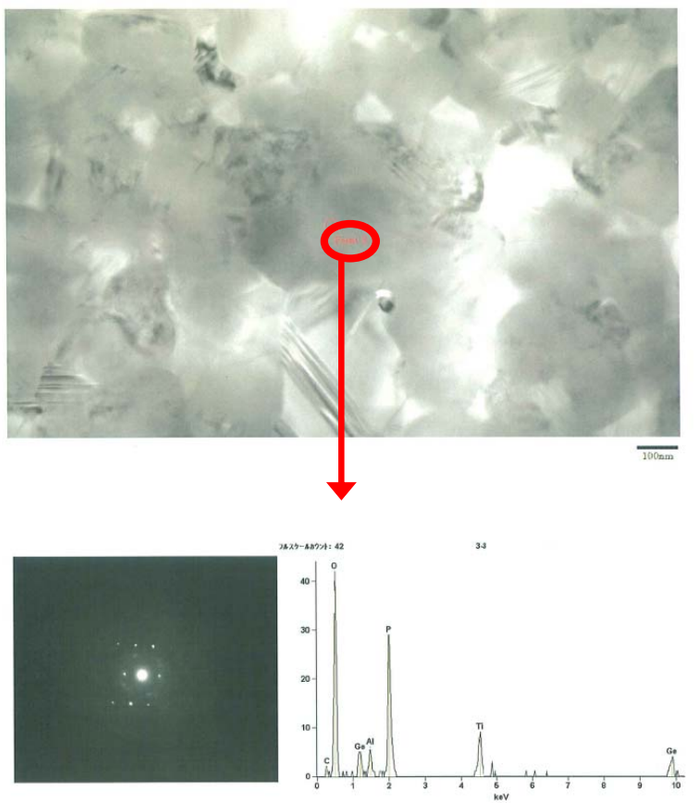
- TEM & EDX




$Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12}$




$AlPO_4$



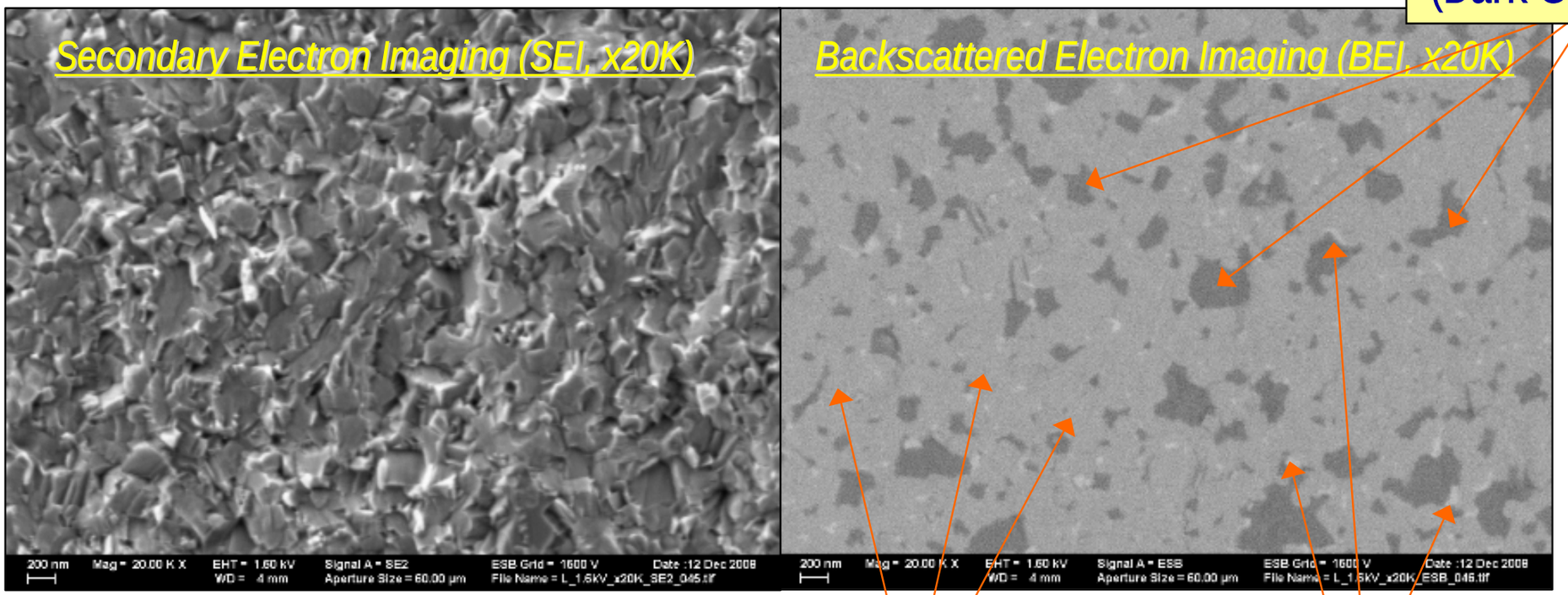

$Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3$

## *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*

$AlPO_4$
(Dark Grey Spot)




$Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12}$
(Light Grey Back Ground)

$Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3$
(White Spot)

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

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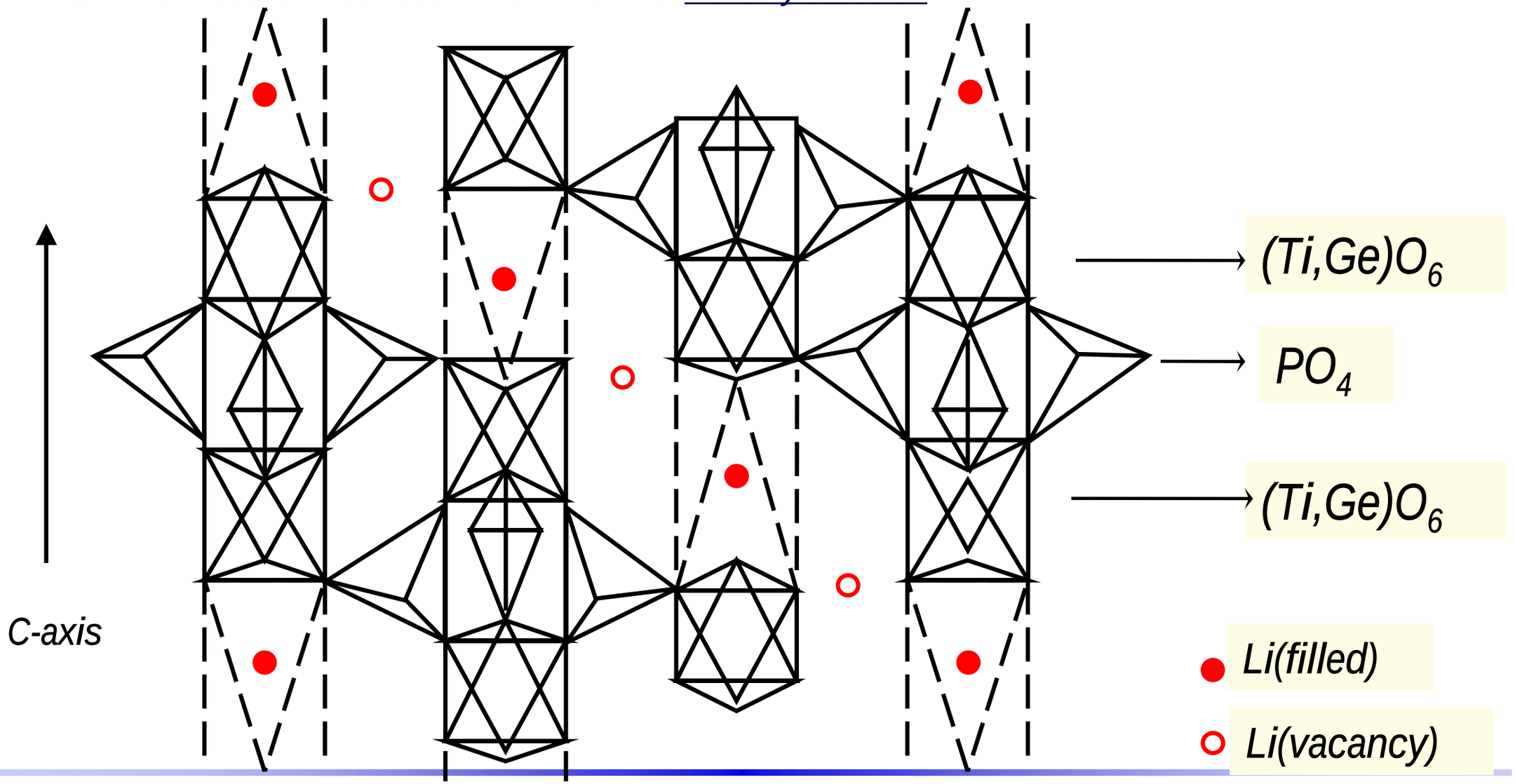
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

- Li Ion Conduction Mechanism in the material: Vacancy Diffusion

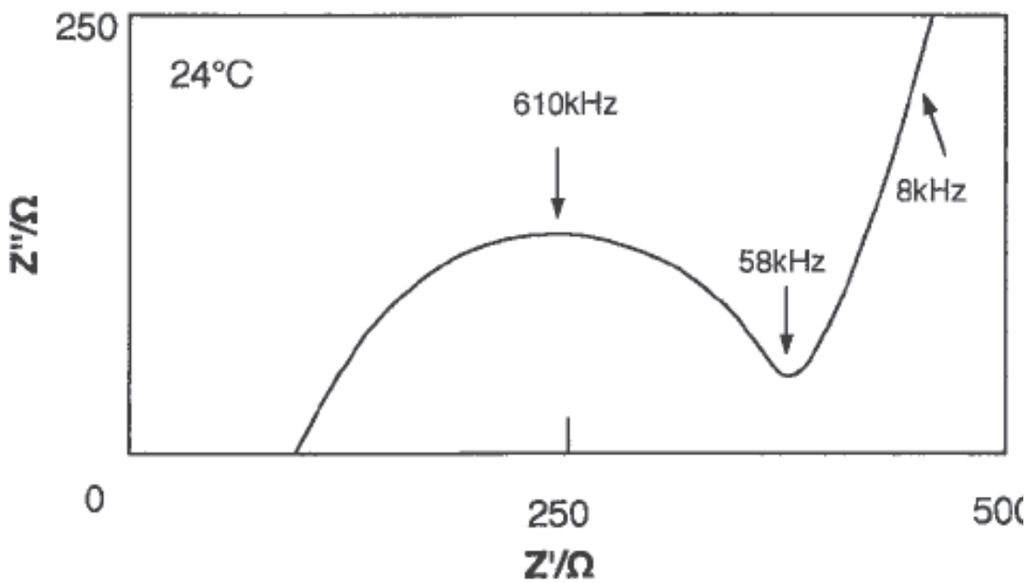


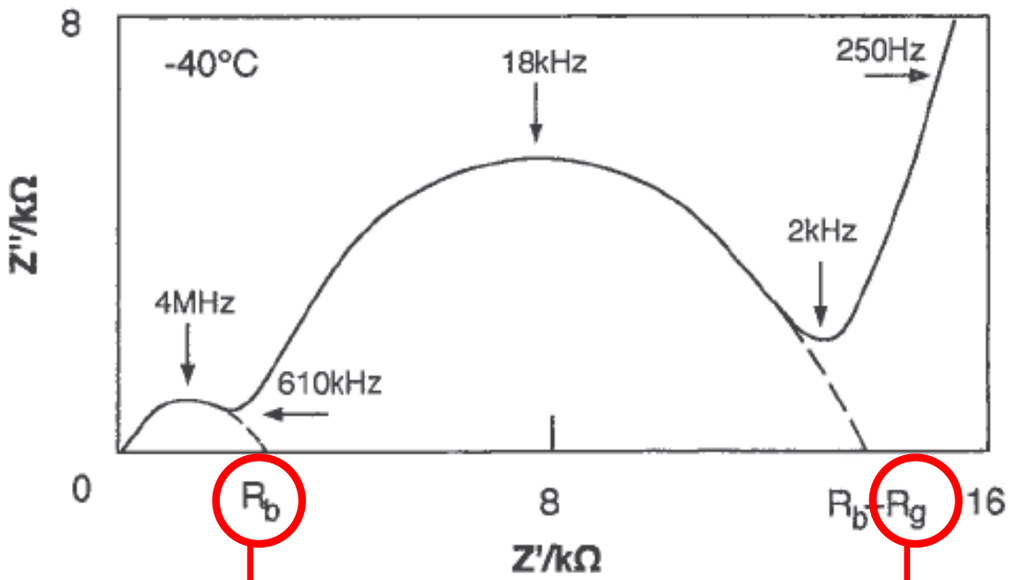
# Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

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

### 3-iii) Composition & Structure

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




Rb: Attributed to "Grain Boundary"

Rg: Attributed to "Bulk of Grain"

*J.Fu, J. Am. Ceram. Soc., 80 (1997) 903-1901*

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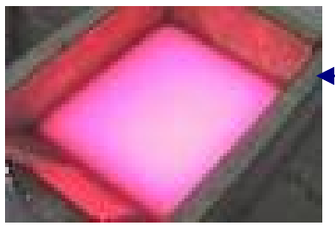
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

### 3-iv) Manufacturing Process (AG-01)

Mixing Raw Materials ($Li_2CO_3$, $Al(PO_3)_3$, $SiO_2$, $H_3PO_4$, $TiO_2$, $GeO_2$)



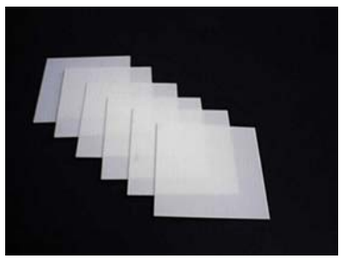
Melting

Glass Drawing & Forming

Crystallization

Mechanical Processing

Lithium-Ion Conductive Glass-ceramics



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

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

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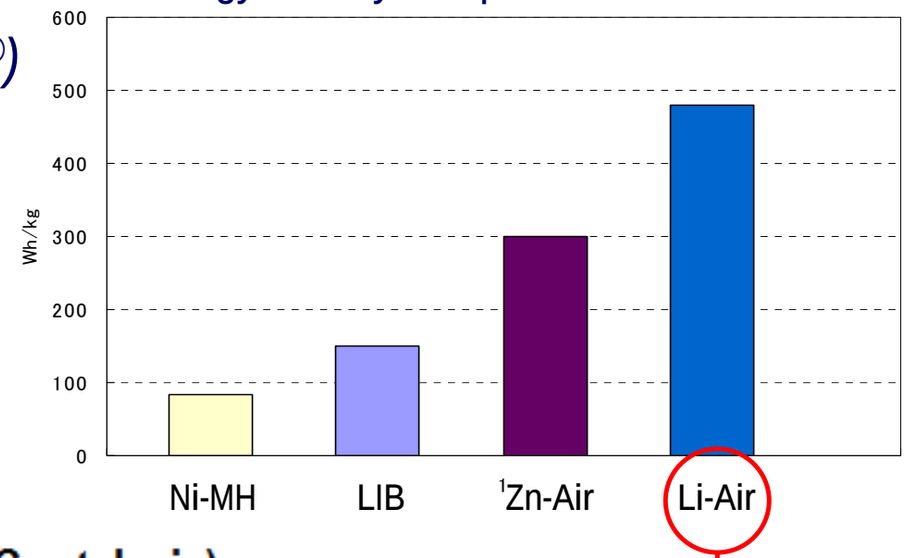
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

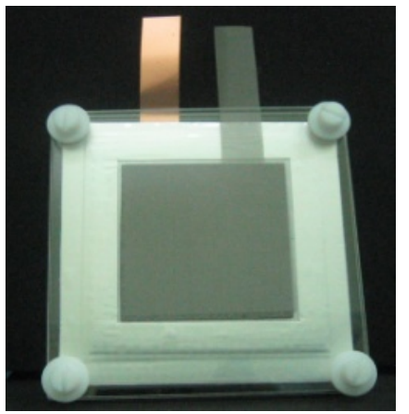
### 3-v) Application

(Solid Electrolyte for Elemental Li / Air Battery)

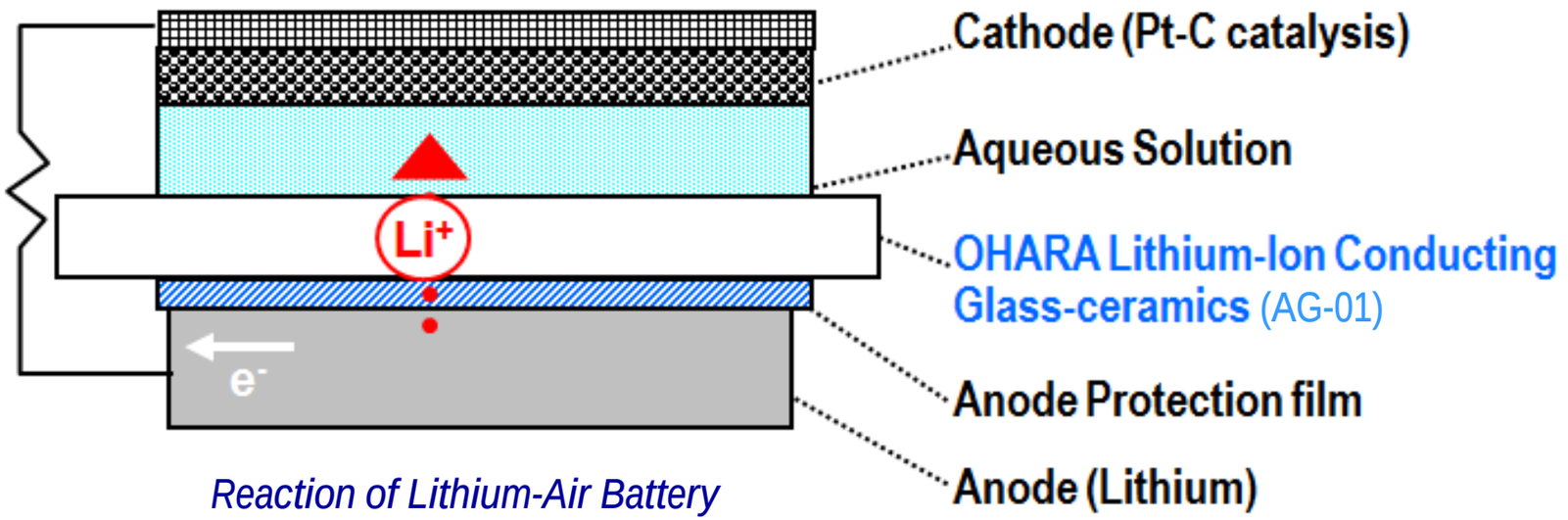
Energy Density Comparison




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



## Li / Air Cell Structure




Reaction of Lithium-Air Battery

Cathode : $O_2+2H_2O+4e^- \rightarrow 4(OH)^-$

Anode : $4Li \rightarrow 4Li^+ + 4e^-$

Cell : $4Li + O_2 + 2H_2O \Leftrightarrow 4LiOH$

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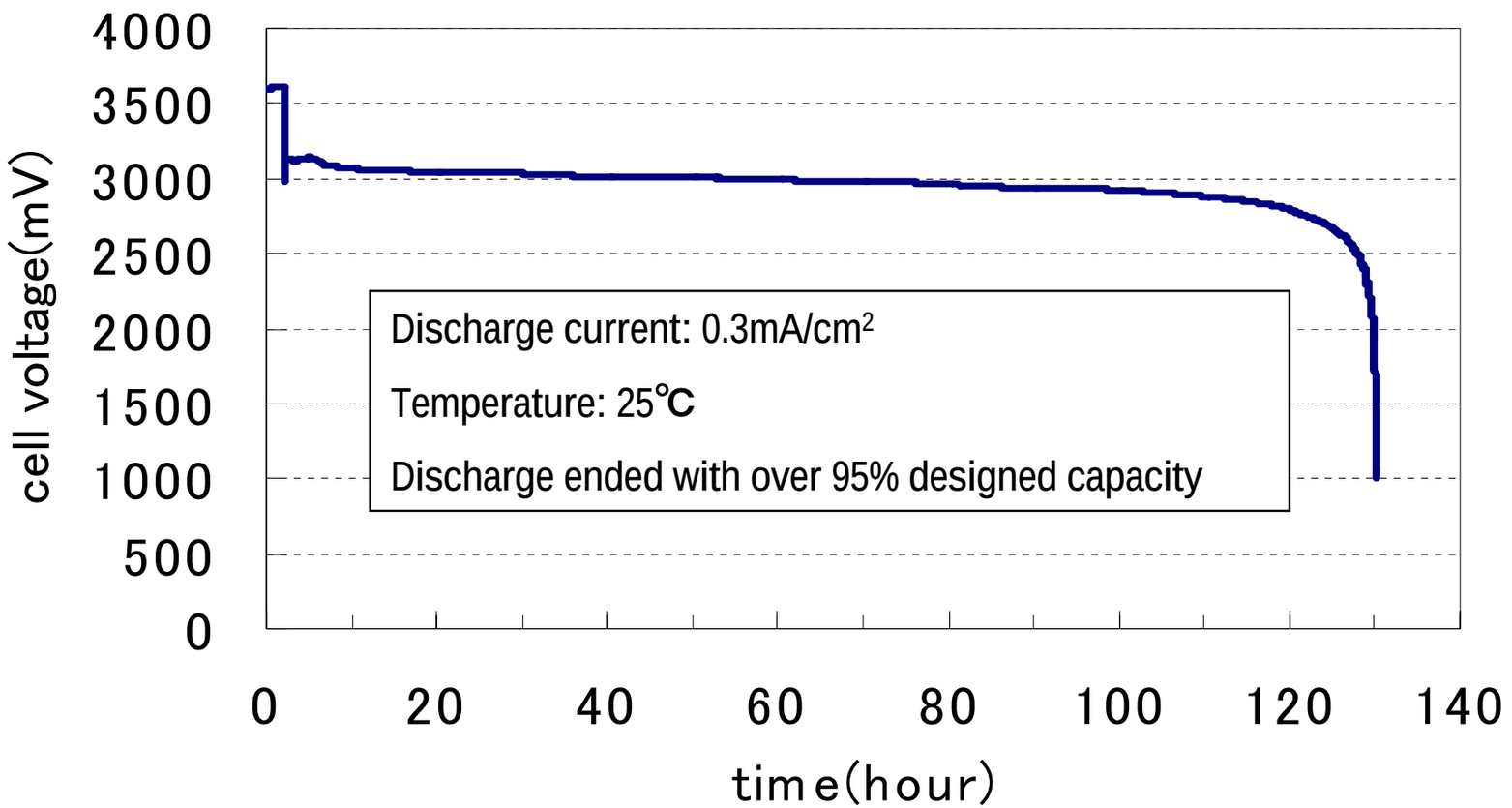
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

#### Li / Air Cell Performance

Discharge curve for the Demonstrative Primary Li / Air Cell



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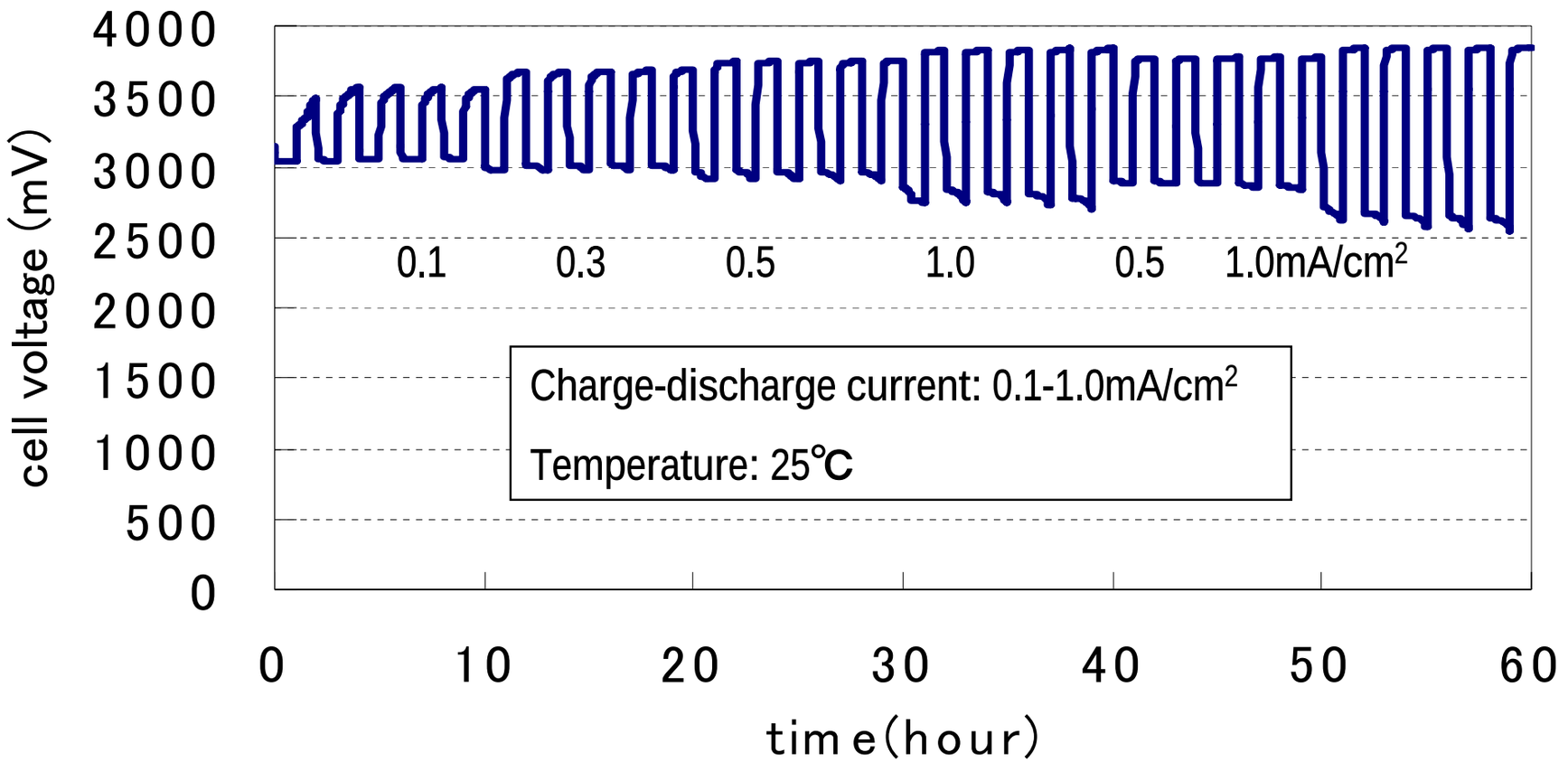
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

### Li / Air Cell Performance

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



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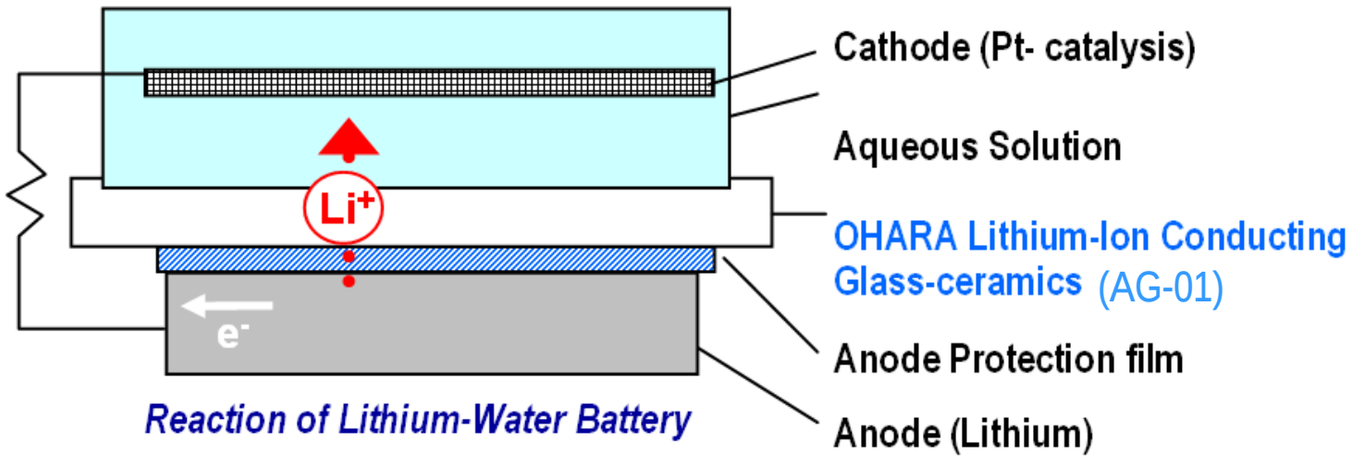
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

## Li / Seawater Cell Structure



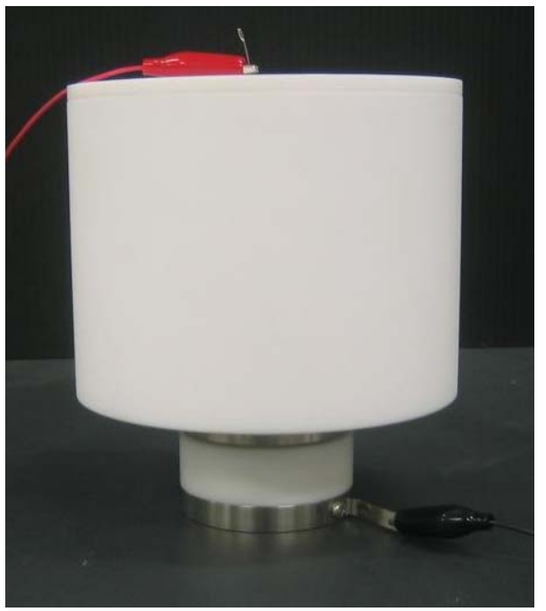

**Reaction of Lithium-Water Battery**

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

Anode : $2Li \rightarrow Li^+ + e^-$

Cell : $2Li + 2H_2O \rightarrow 2LiOH + H_2$

Li / Seawater Prototype Cell
for solid electrolyte evaluation
(Using Sq.1" LIC-GC® AG-01)



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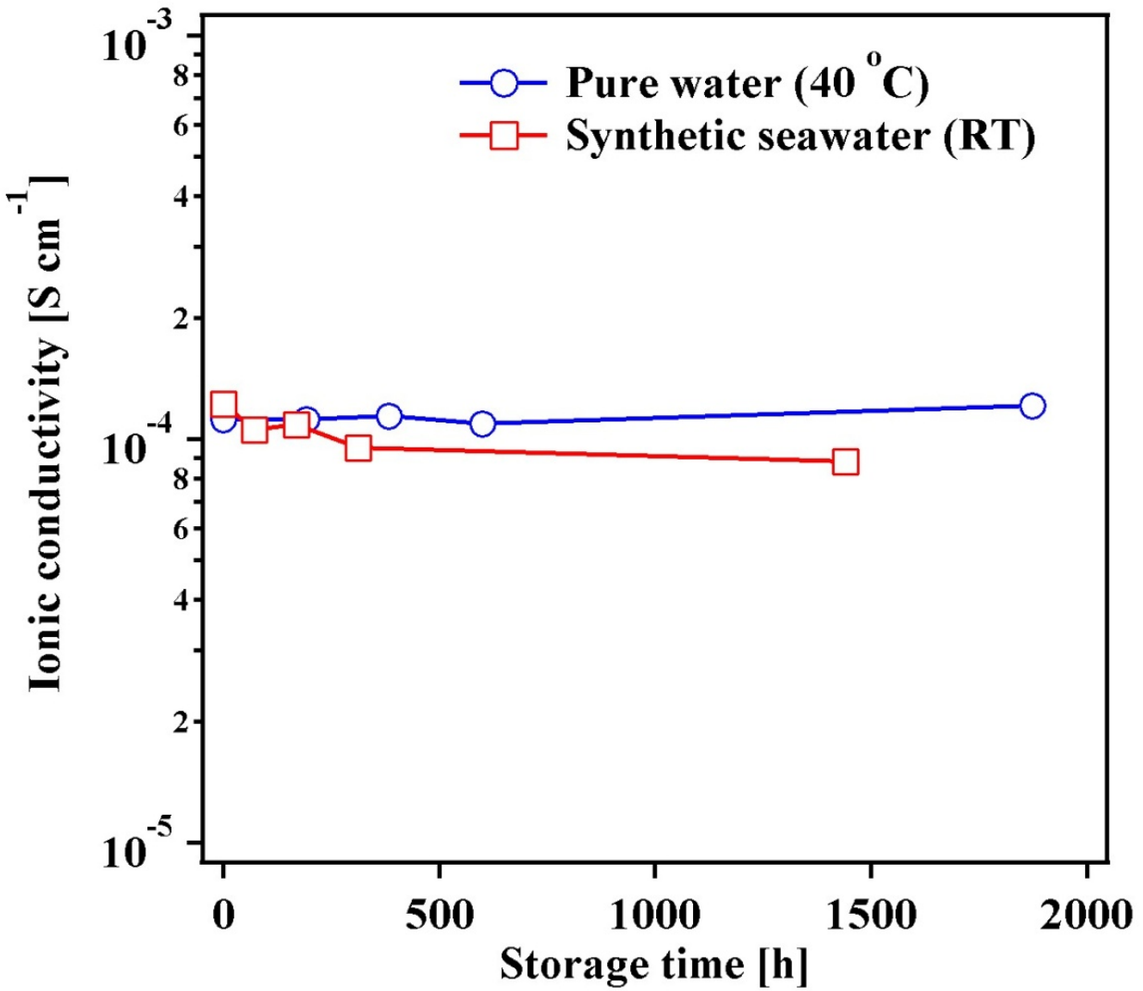
## 3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

### Water / Seawater Resistivity of LIC-GC® AG-01 in Static test.



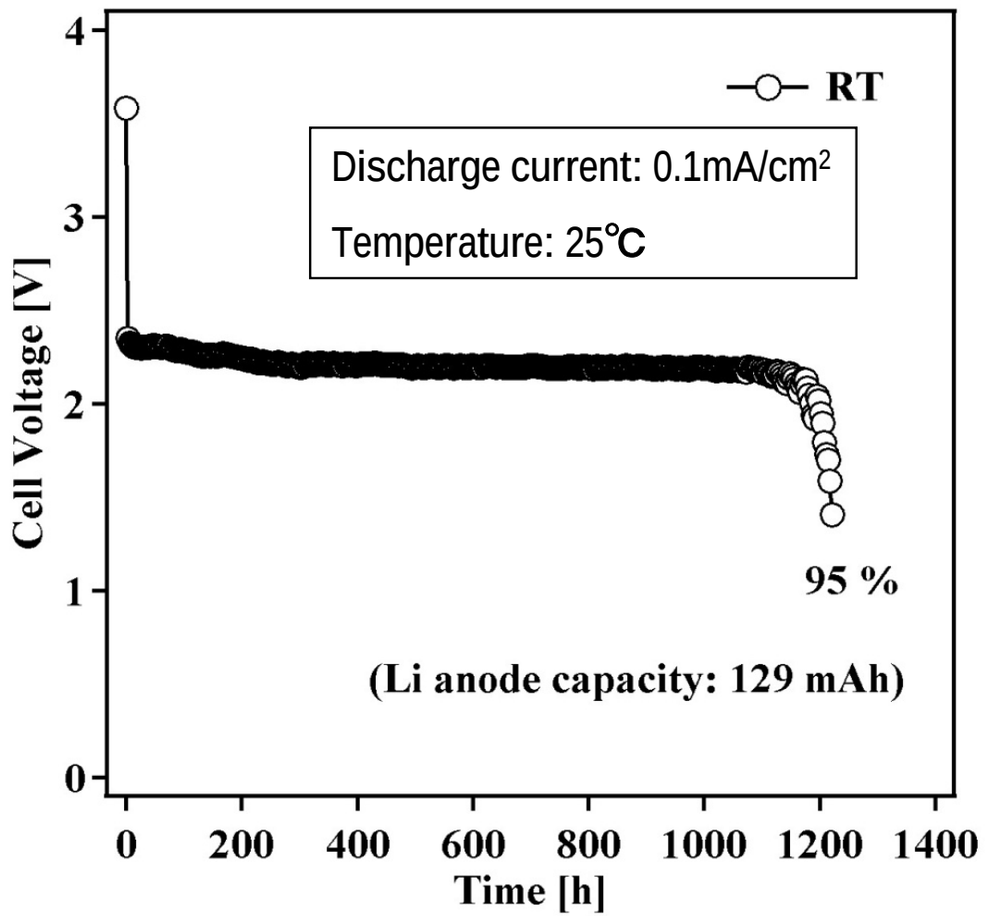
OHARA®

## 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




30days 50days

## *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."*

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*End of the Presentation.*

*Thank you for your listening.*