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

Kousuke Nakajima [a], Takashi Katoh [a],
Yasushi Inda [a], Brion Hoffman [b]

[a]OHARA-INC., 1-15-30 Oyama, Chuo-ku, Sagamihara-shi, Kanagawa 252-5286, Japan
[b]OHARA CORPORATION, 23141 Arroyo Vista,Suite 200,
Rancho Santa Margarita, CA 92688, United States

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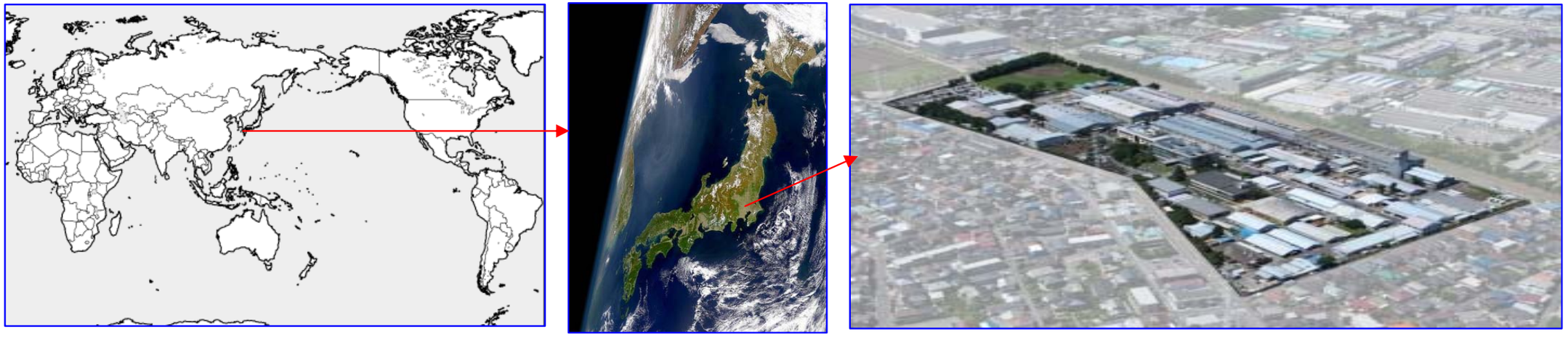
4) Conclusion
5) Acknowledgement

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)

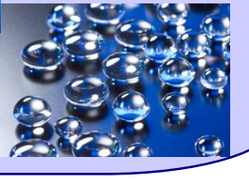


Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

1) Introduction of OHARA Group

< OHARA Group Business Domain >

Optical Business Domain

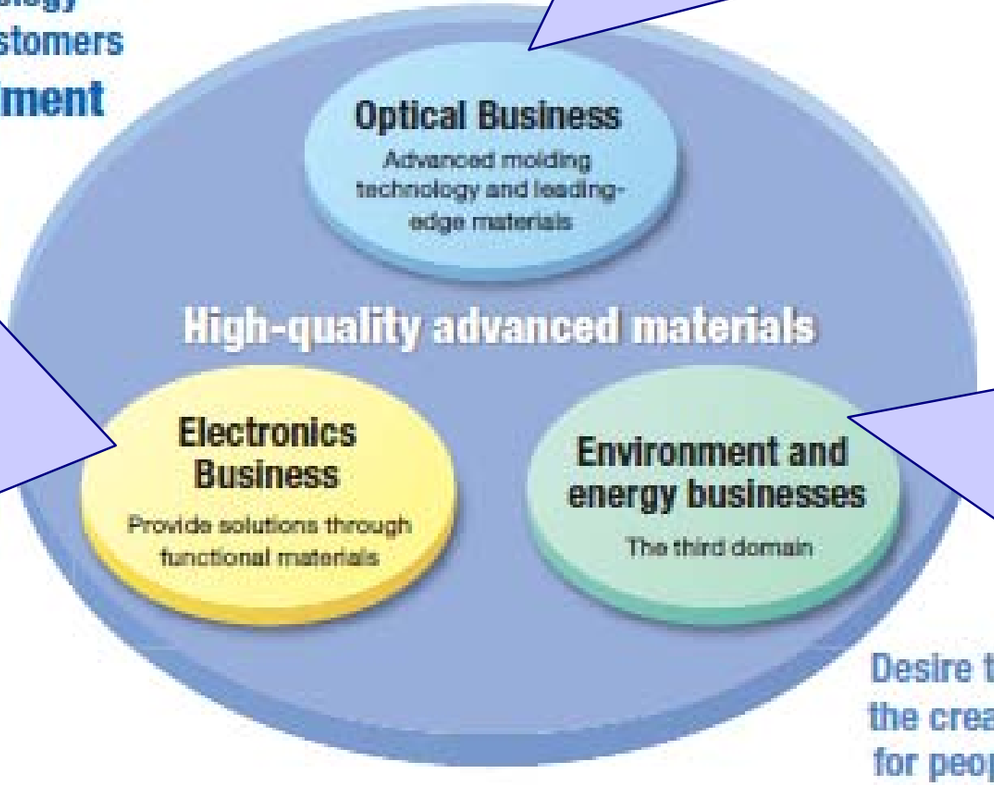


- Pressings, Blocks
- Low Tg Optical Glass

For Digital Camera, Microscope, Telescope, etc.

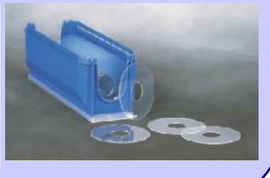
Innovating Technology Together with Customers

"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

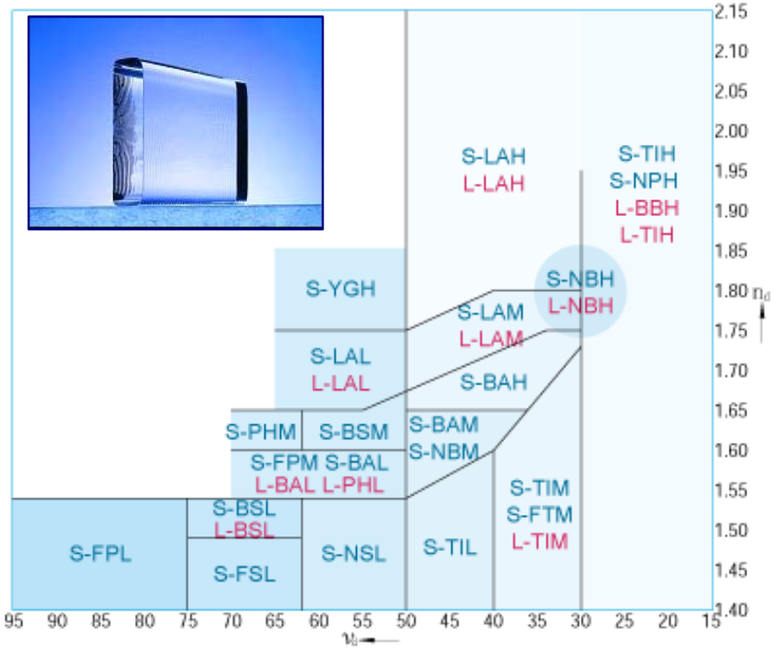
- Lithium Ion Conductive Glass-ceramics

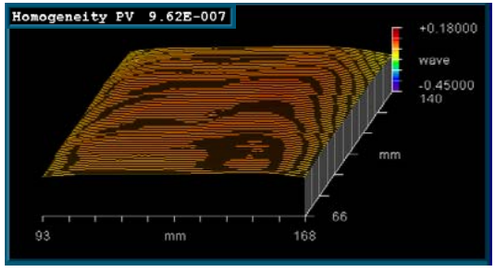
Desire to contribute to the creating the future for people and society

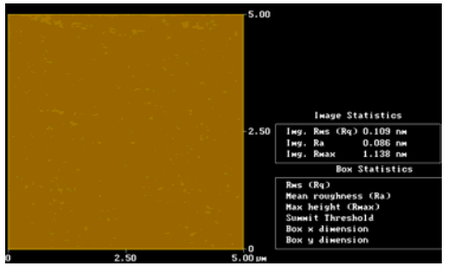
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

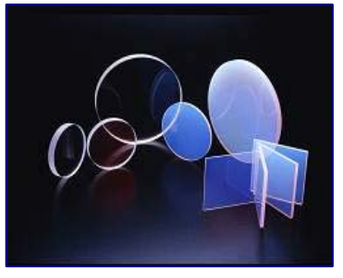
2) Technologies of OHARA Group

- 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







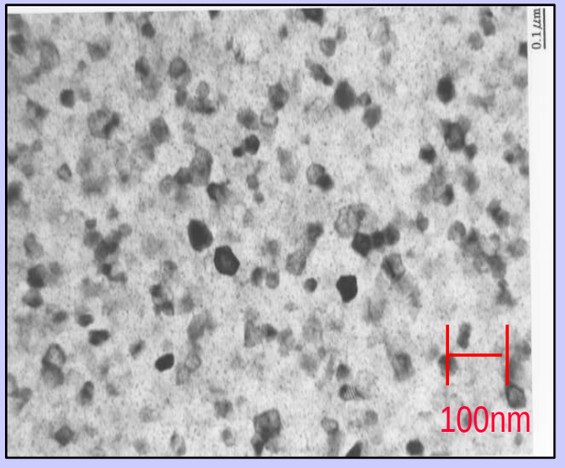


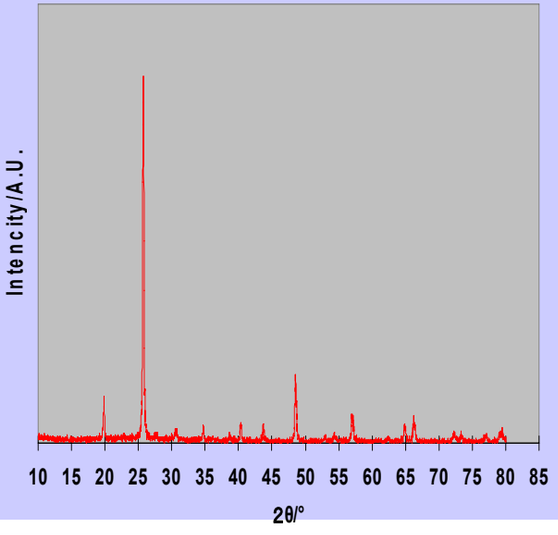
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

2) Technologies of OHARA Group

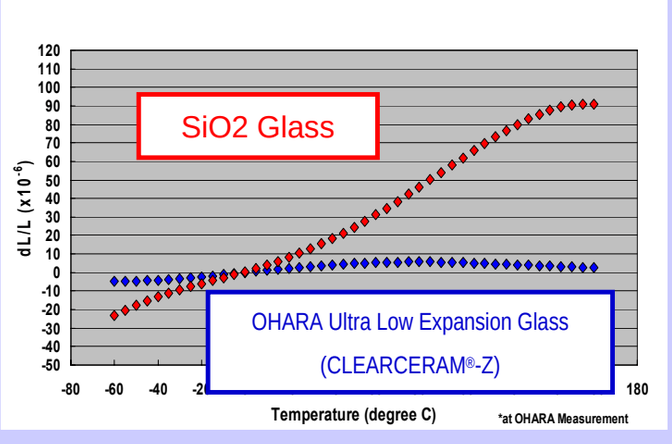
- Glass-ceramics Technology

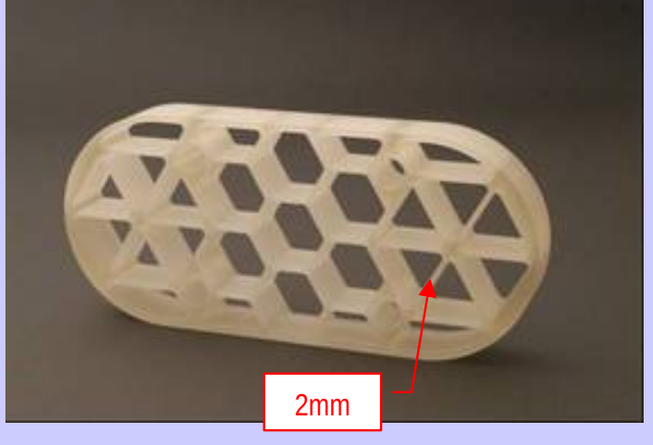
- Composition / Structure: Nono-scale aggregates of poly-crystalline particles are dispersed among amorphous glass matrix

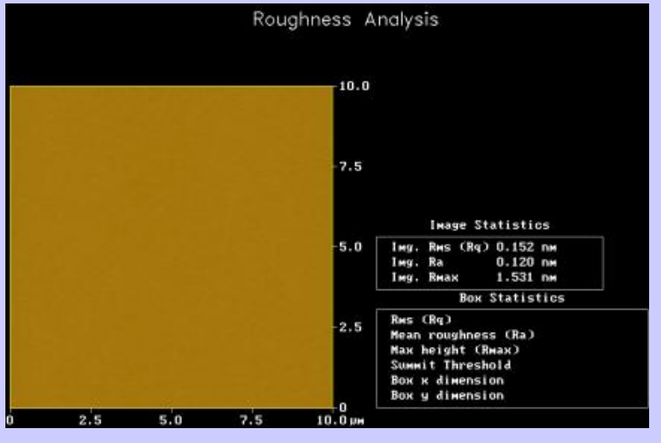




- Benefits: Added properties (values) to the original glass, with Improved Mechanical Strength and Processability







OHARA®

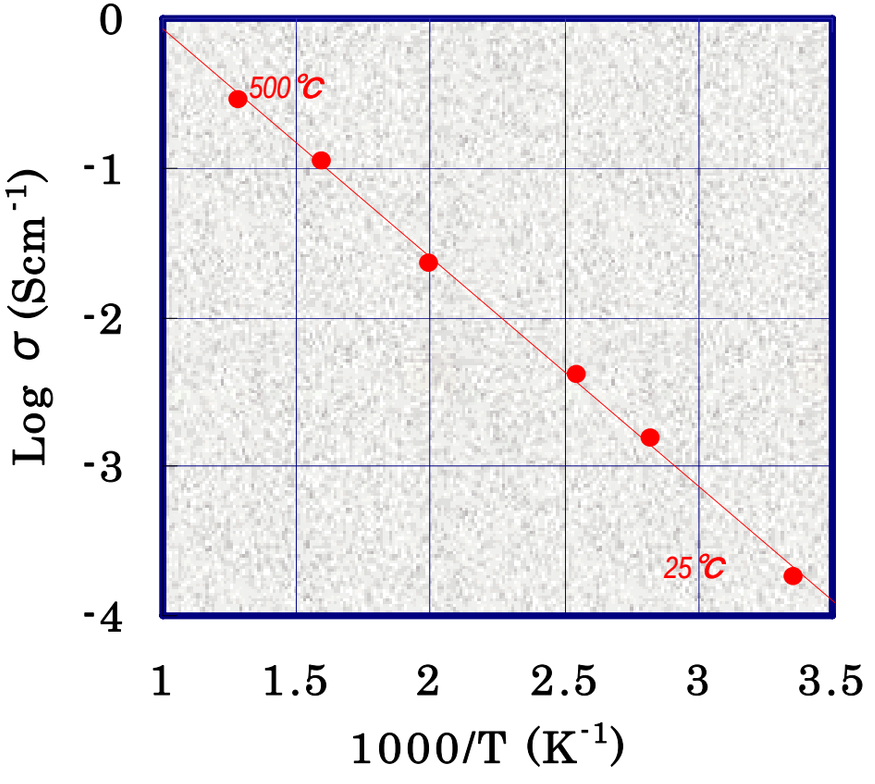
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

OHARA®

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:

AG-01 Membrane
in Dia.2”x250um thickness

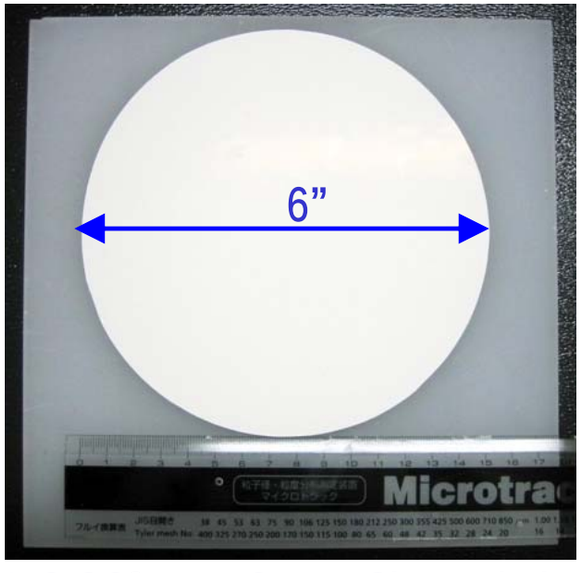
a.) AG-01 melted & polished plates

- 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



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

< 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

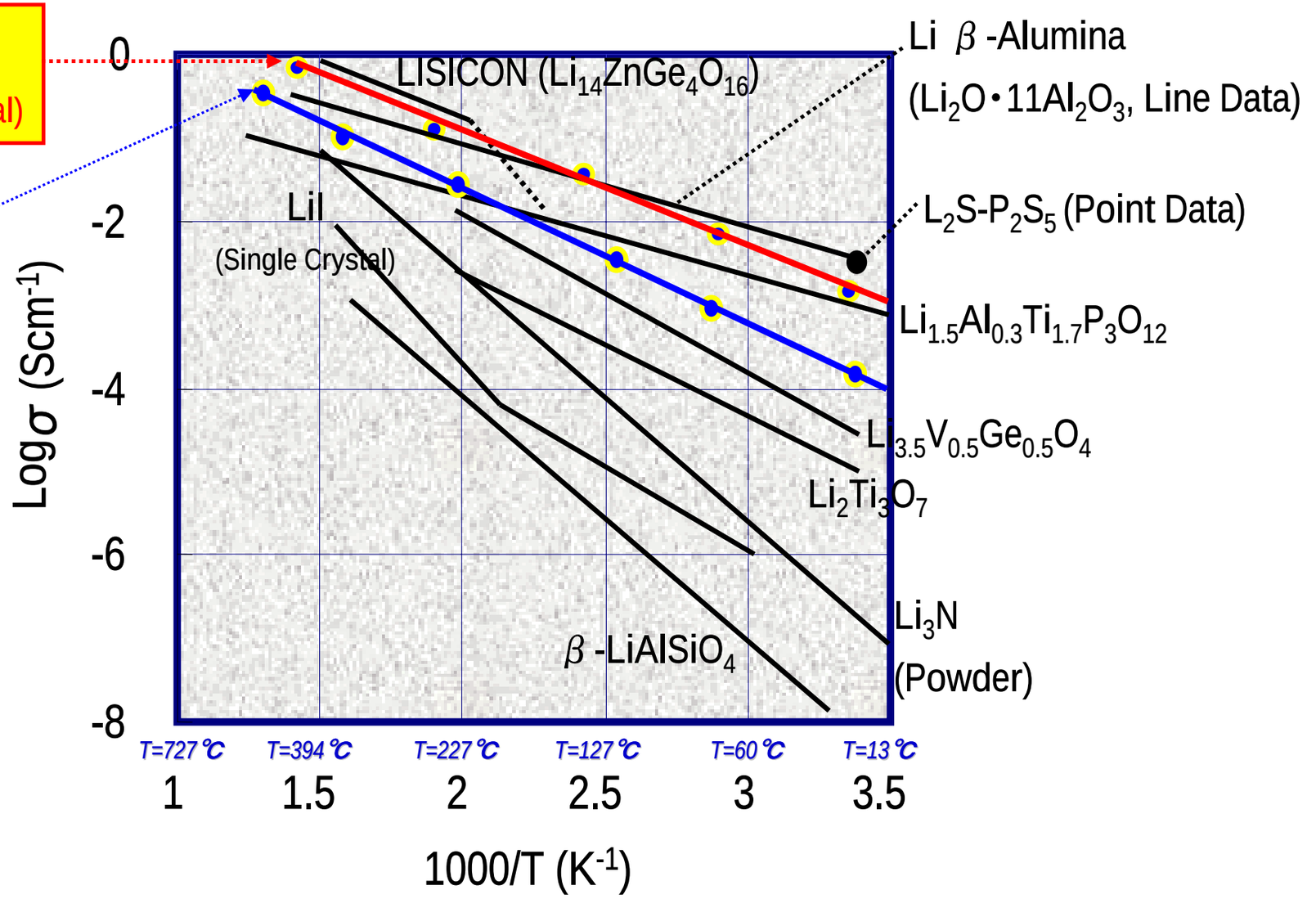
OHARA®

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

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

LIC-GC®
(Original Powder Material)

LIC-GC®
(AG-01 Membrane)

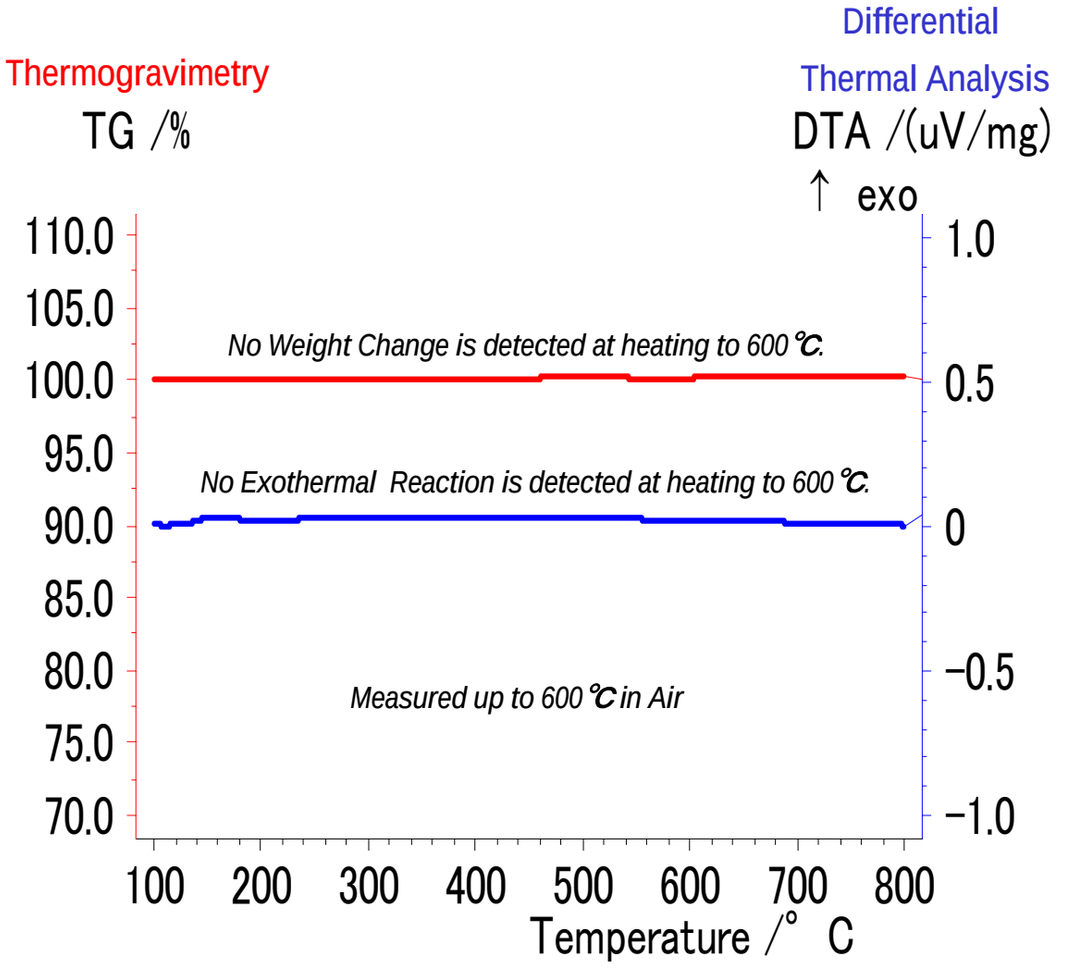


Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

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

3-i) Main Feature

Thermally Stable up to 600℃



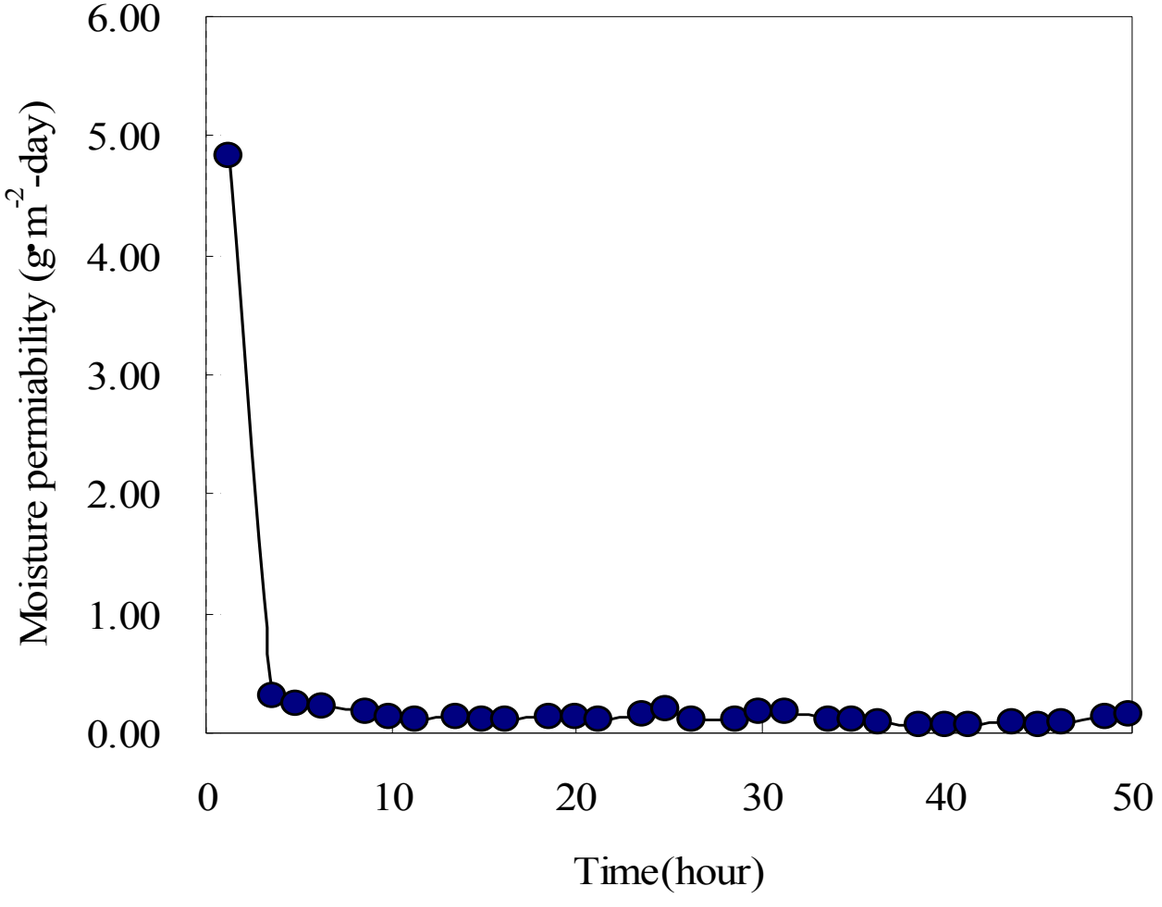
Nonflammable, Can be Handled in Air.

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

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

3-i) Main Feature

Blocking moisture penetration
(Moisture Permeabilitv Measurement)



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

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	94×10^{-7}/degree C (30 ~ 350degree C)
		82×10^{-7}/degree C (350 ~ 600degree C)

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

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

} $Li_{1+x+3z}Al_x(Ti,Ge)_{2-x}Si_{3z}P_{3-z}O_{12}$

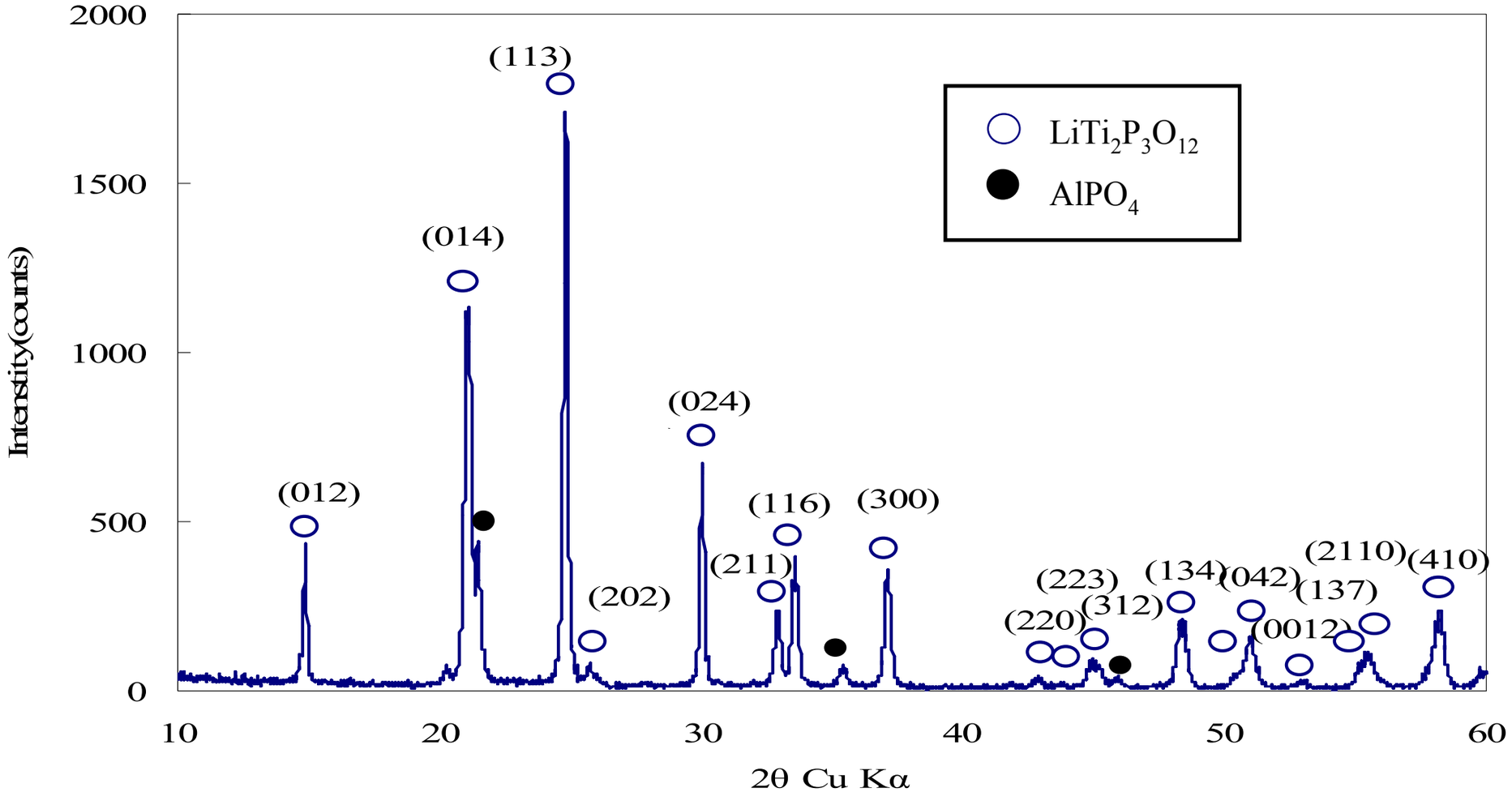
Sub Crystal Phase: $AlPO_4$

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 (AG-01)

- X-Ray Diffraction

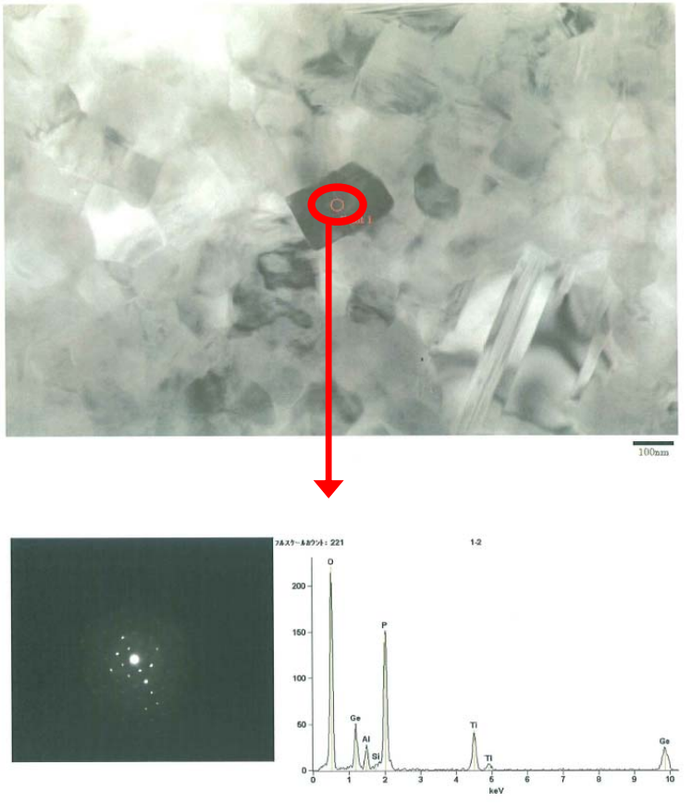


Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

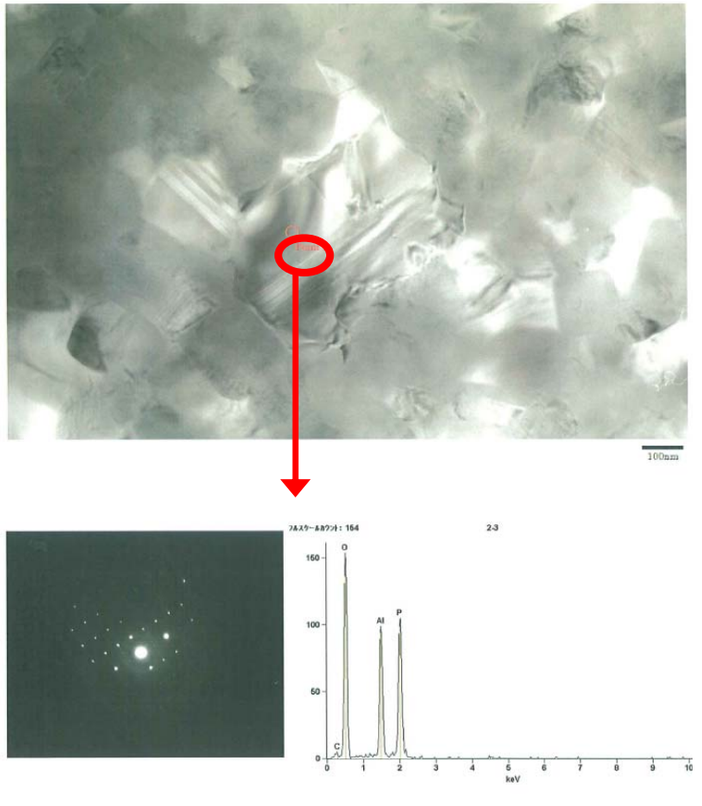
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

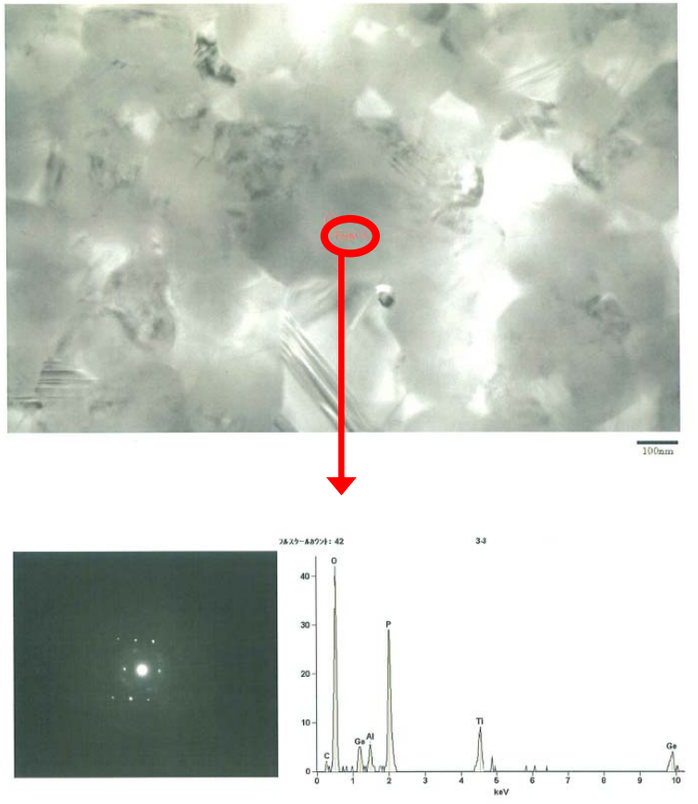
- TEM & EDX



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



$AlPO_4$



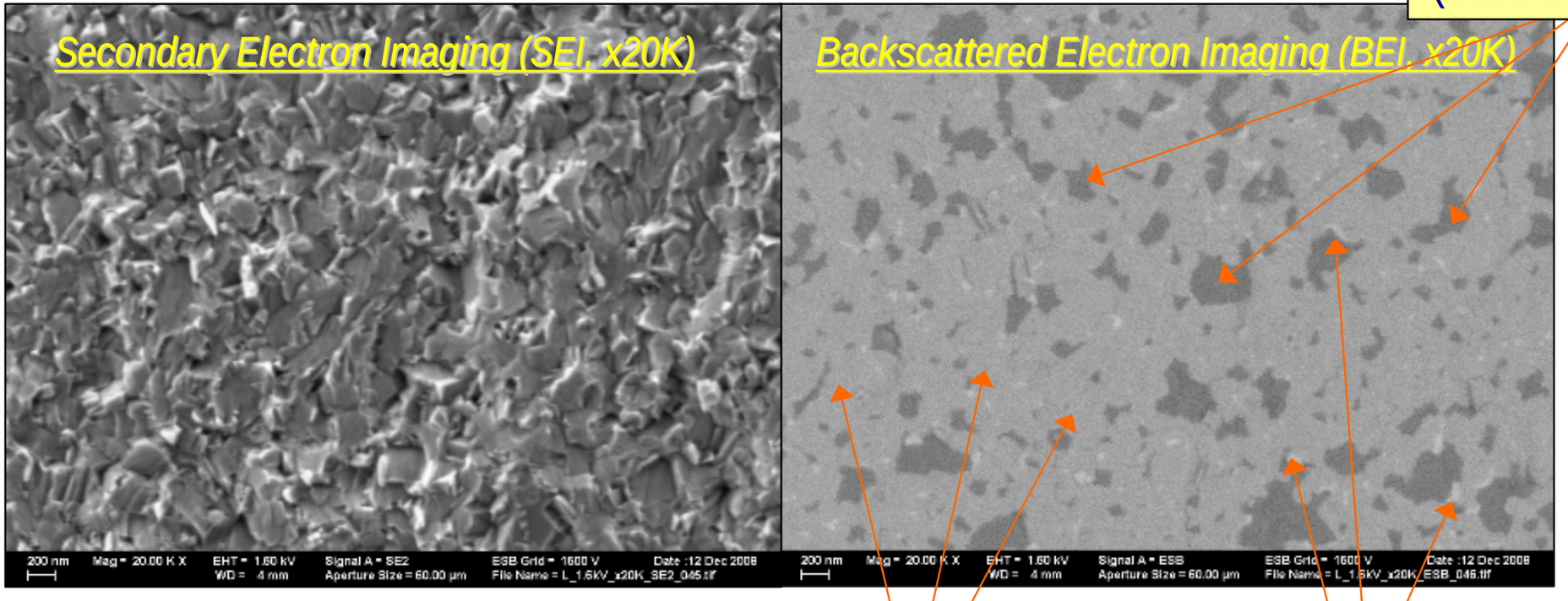
$Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3$

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



$AlPO_4$
(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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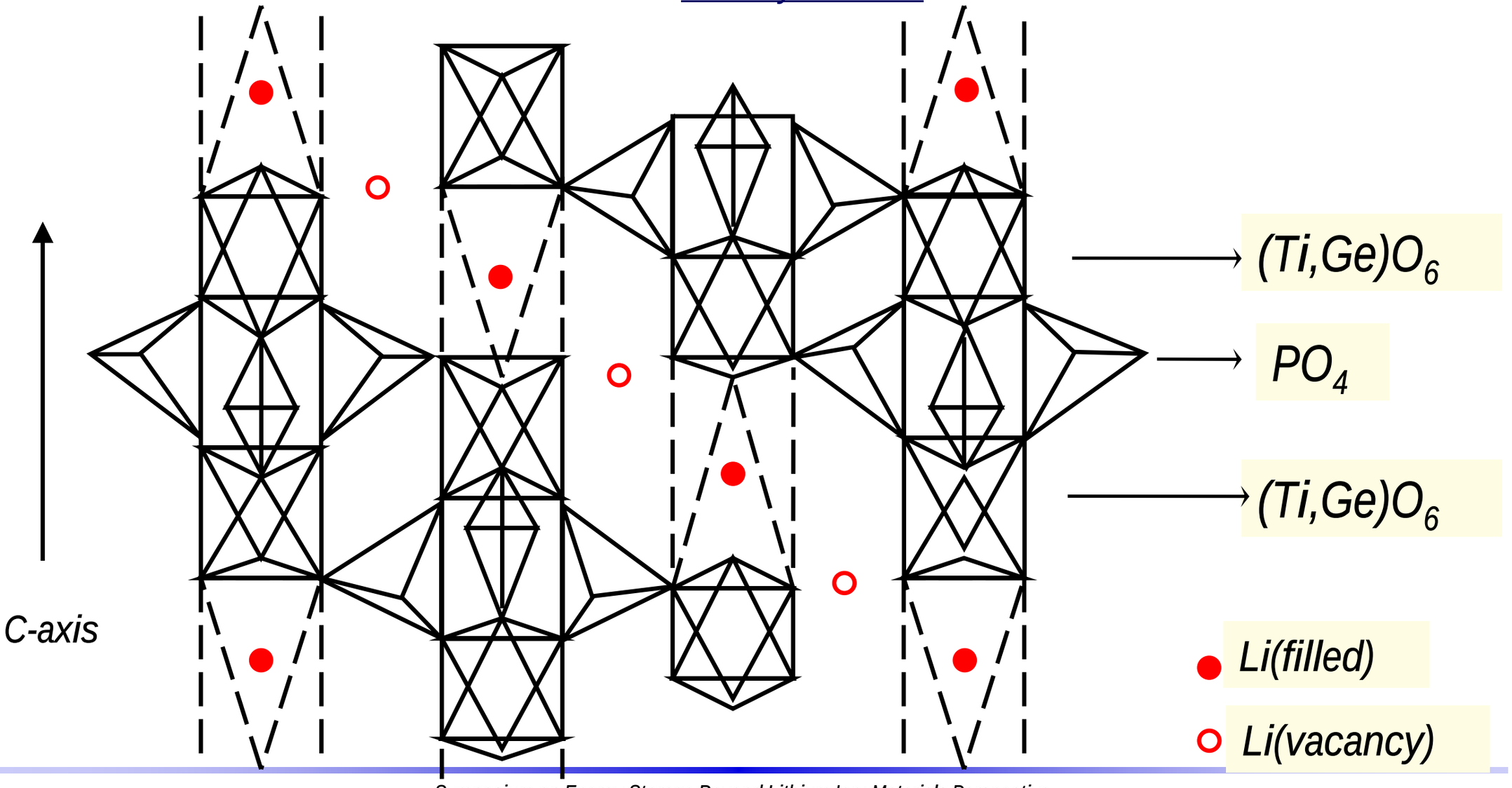
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

- Li Ion Conduction Mechanism in the material: Vacancy Diffusion

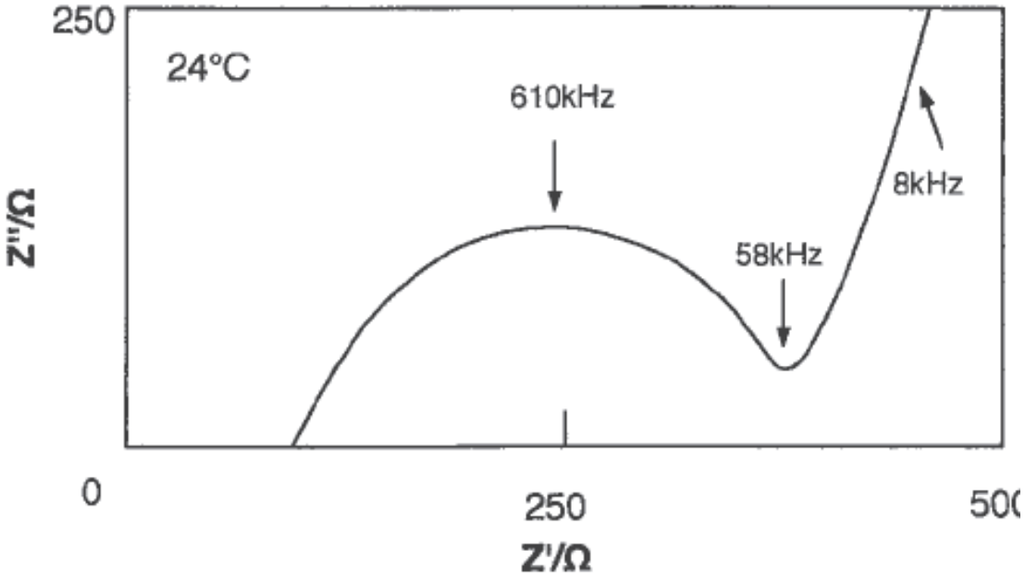


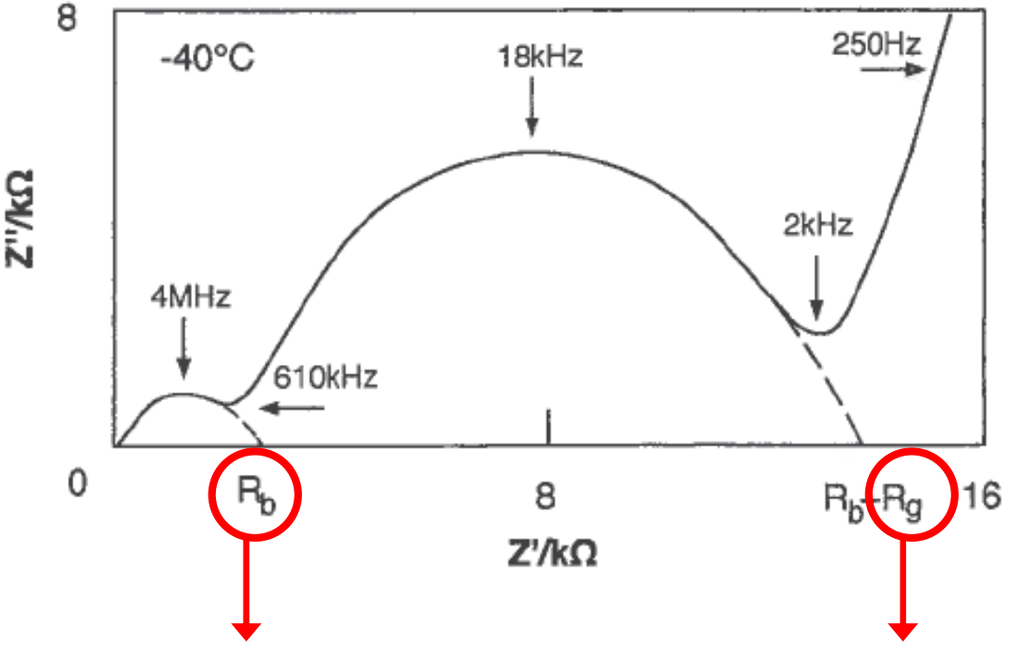
Lithium Ion Conductive Glass Ceramics (LIC-GC®): Properties and Application in Lithium Metal Batteries

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"

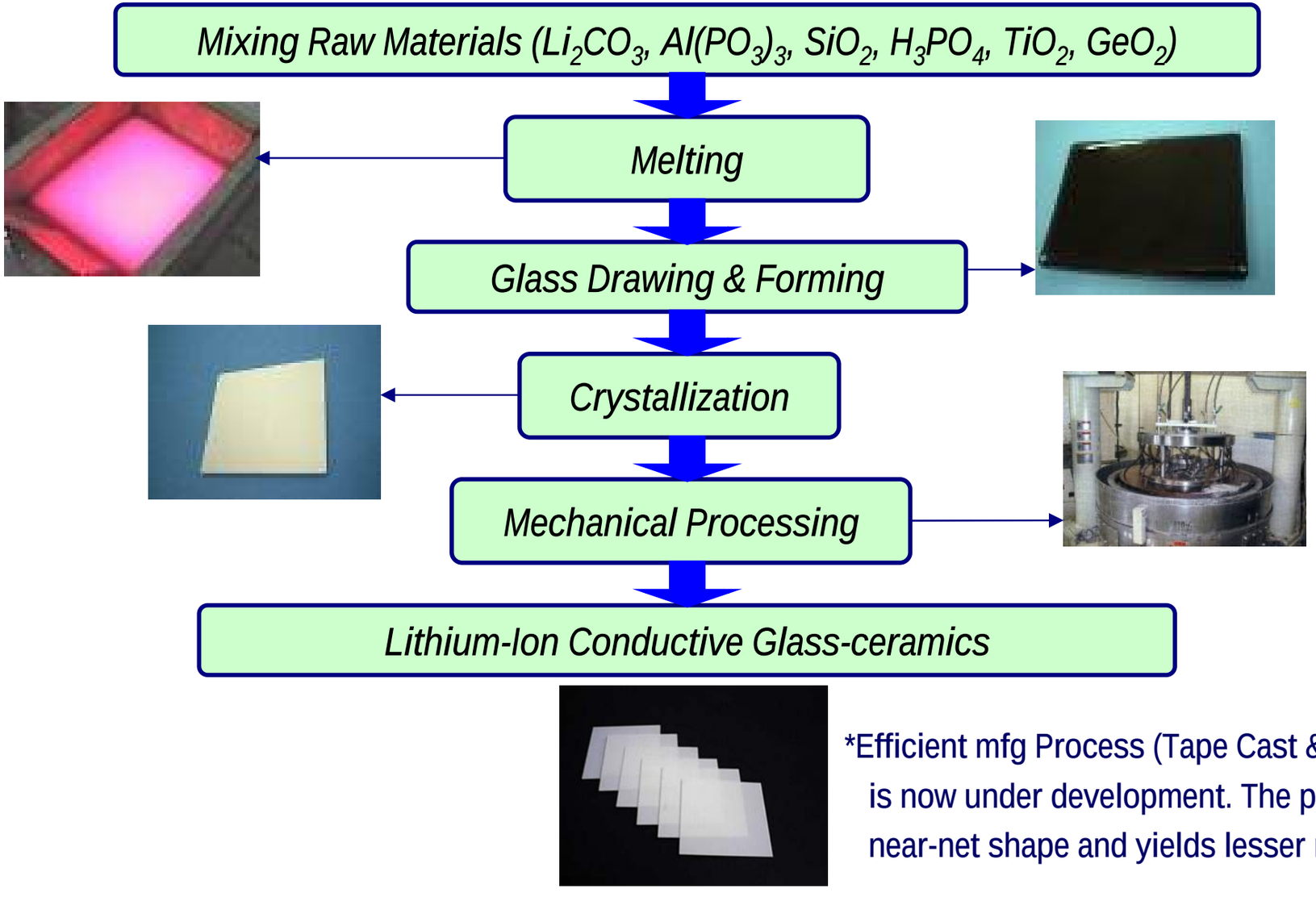
Rg: Attributed to "Bulk of Grain"

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

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

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

3-iv) Manufacturing Process (AG-01)



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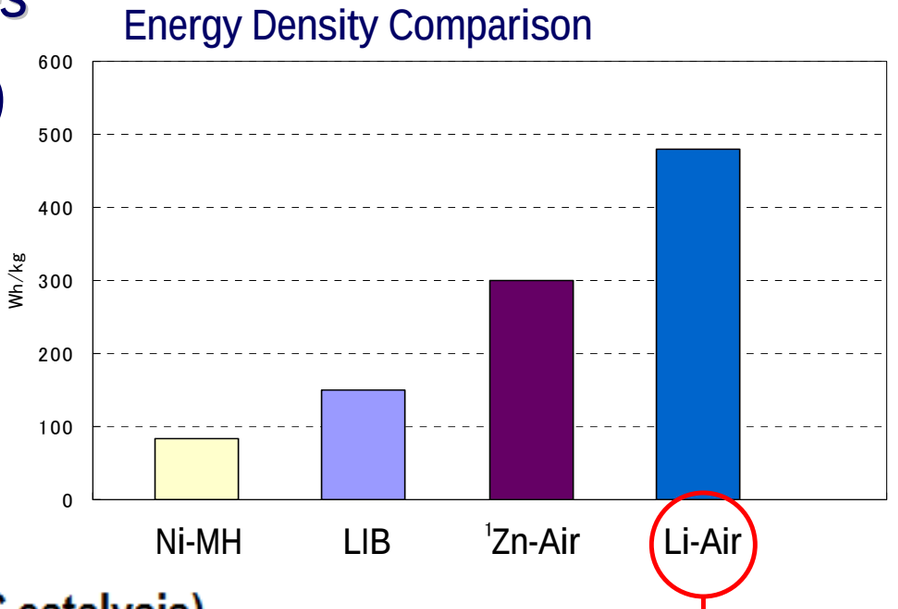
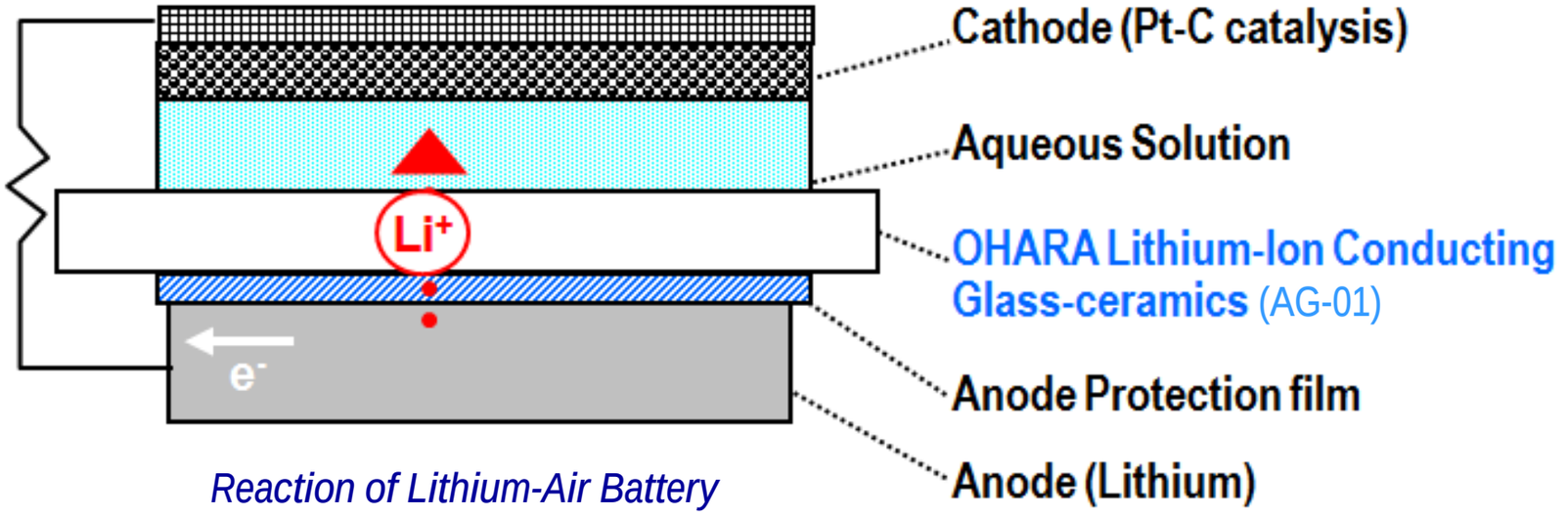
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

3-v) Application

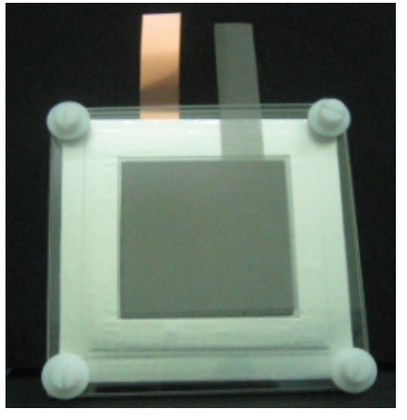
(Solid Electrolyte for Elemental Li / Air Battery)



Li / Air Cell Structure



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



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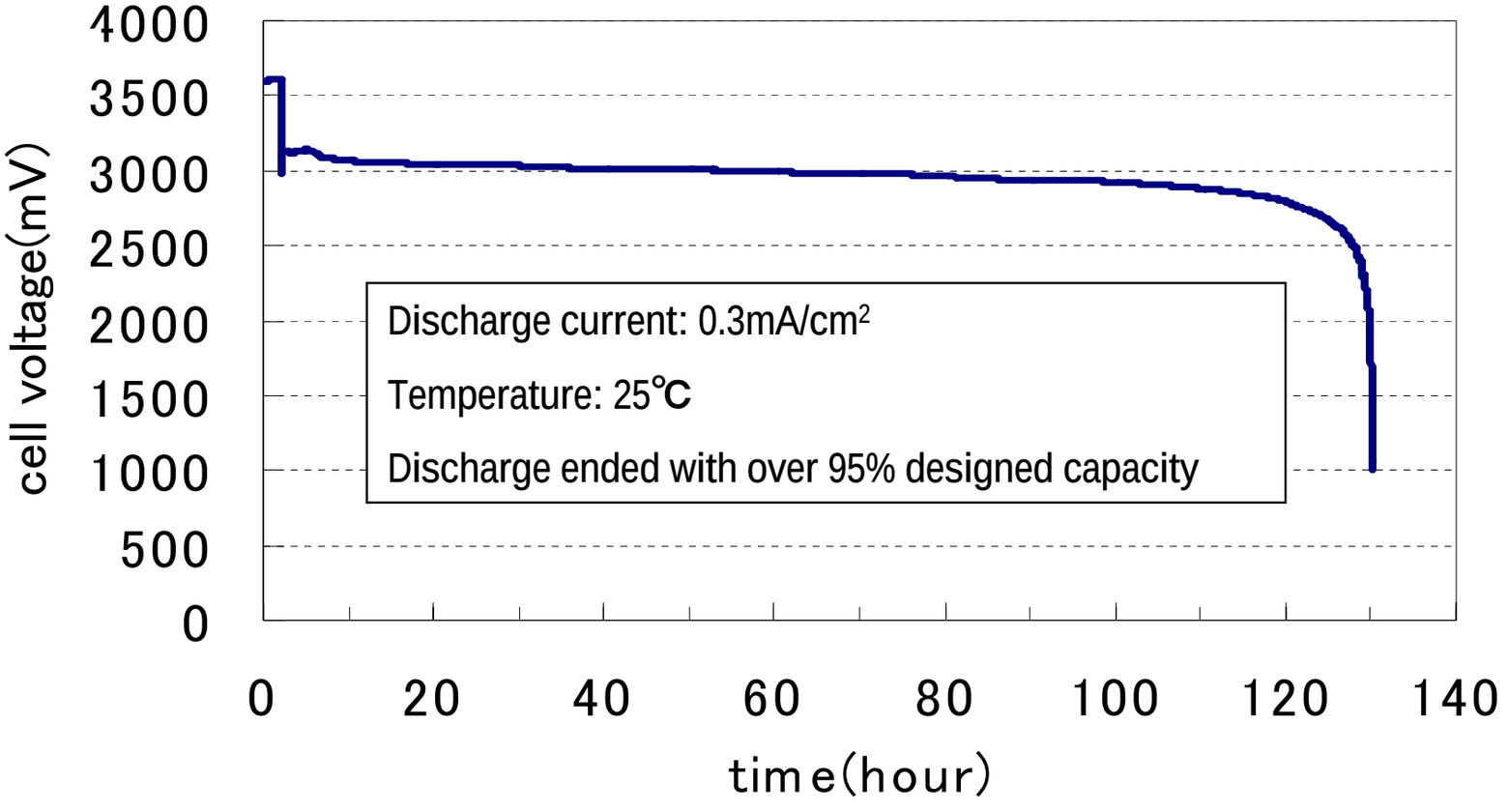
3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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

Li / Air Cell Performance

Discharge curve for the Demonstrative Primary Li / Air Cell



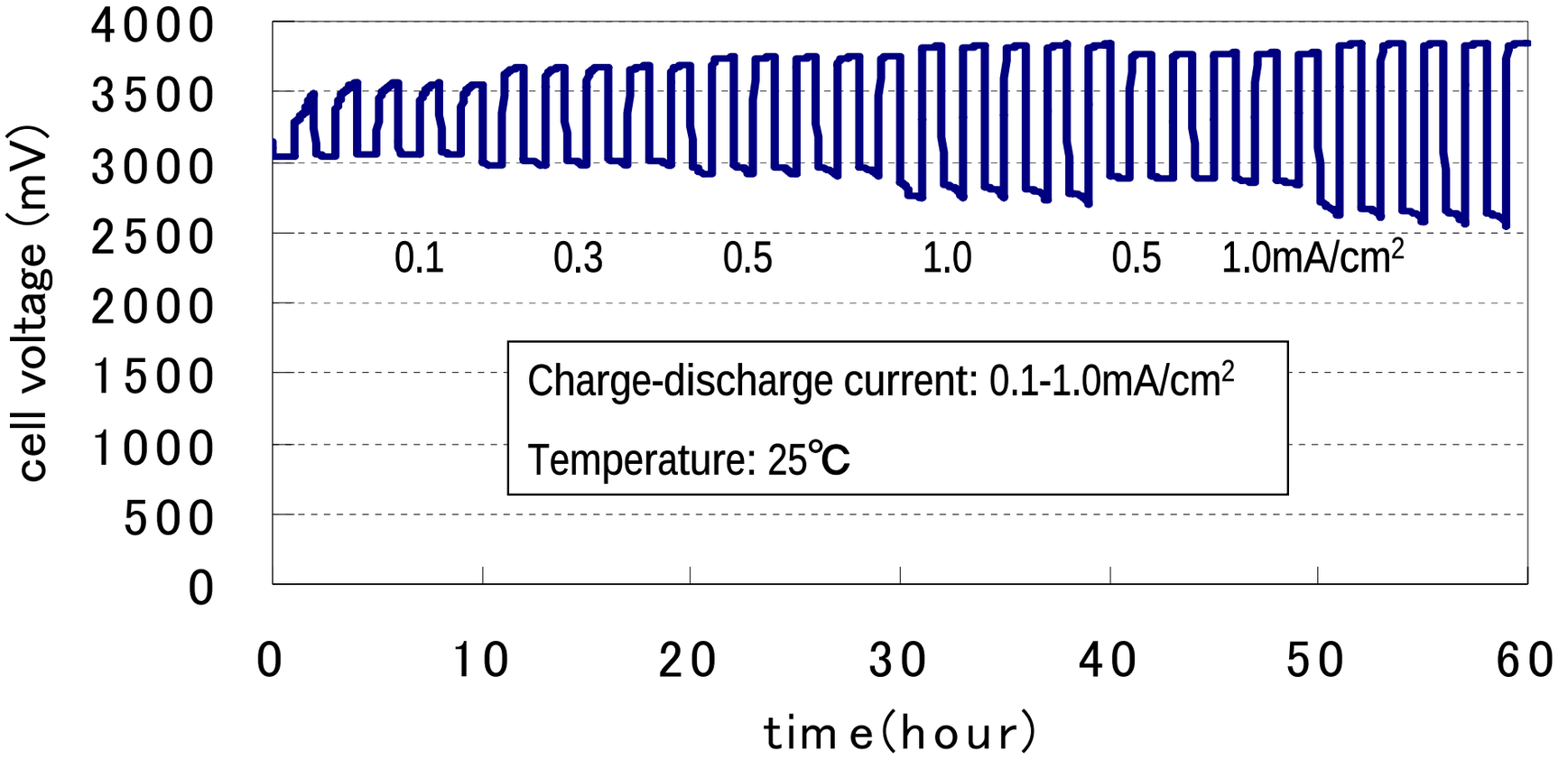
OHARA®

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

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

Li / Air Cell Performance

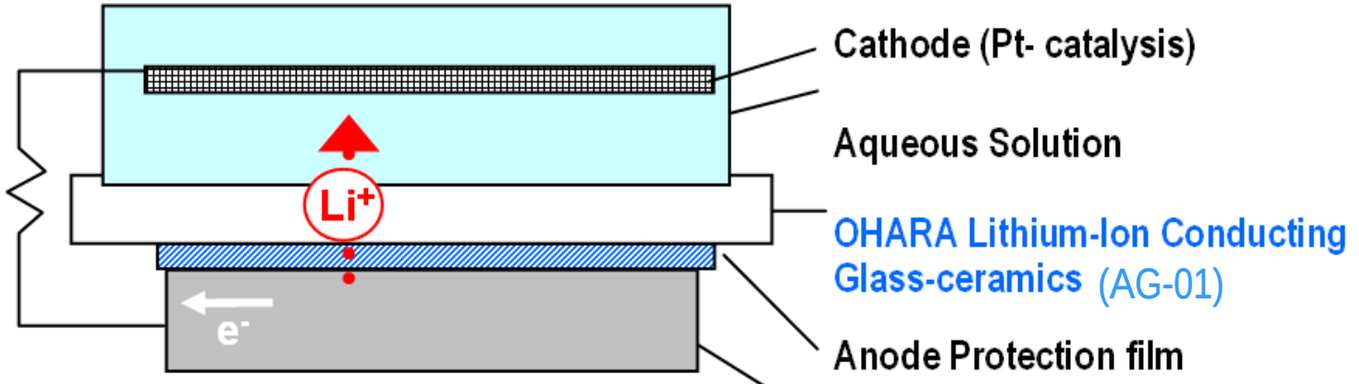
Charge-Discharge Curve for the Demonstrative Secondary Li/Air Cell



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

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

Li / Seawater Cell Structure



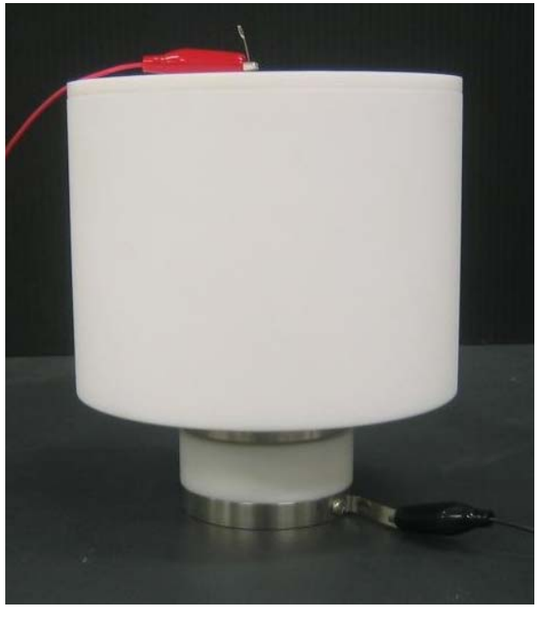
Reaction of Lithium-Water Battery

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)

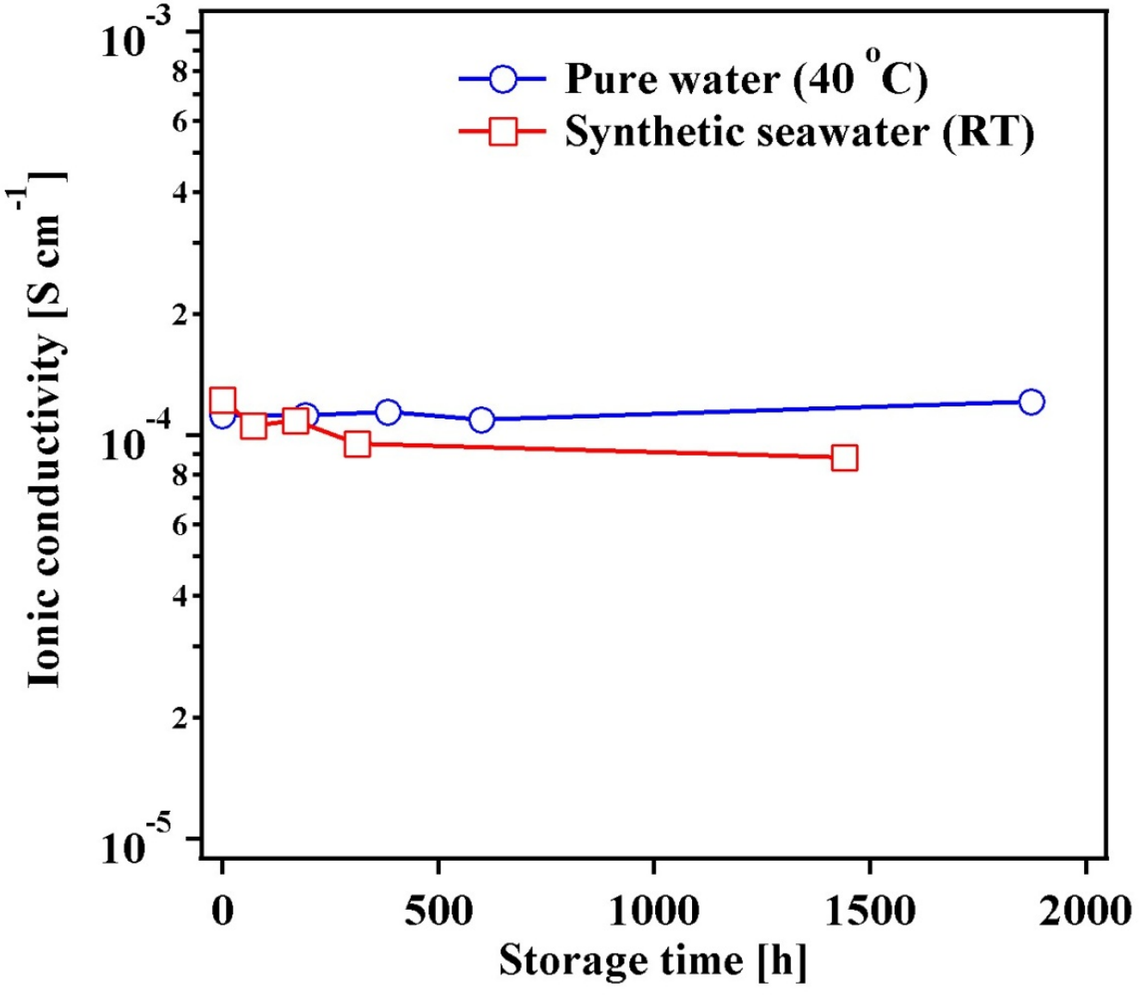


OHARA®

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.

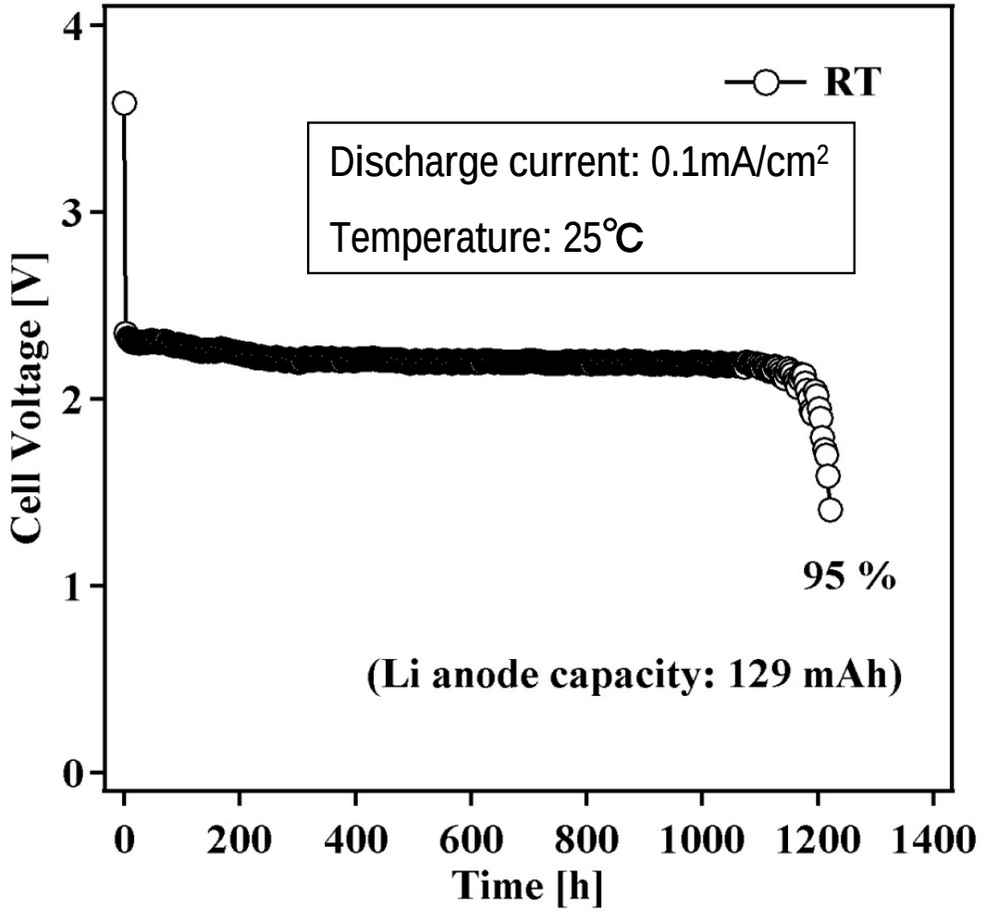


3) The Lithium Ion Conductive Glass Ceramics (LIC-GC®)

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."

End of the Presentation.

Thank you for your listening.