

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

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Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



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Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



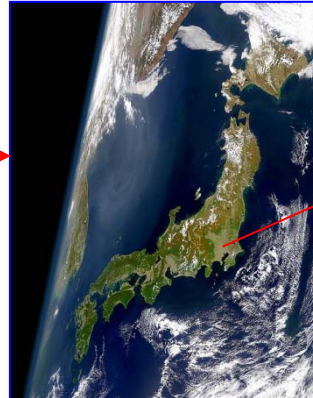
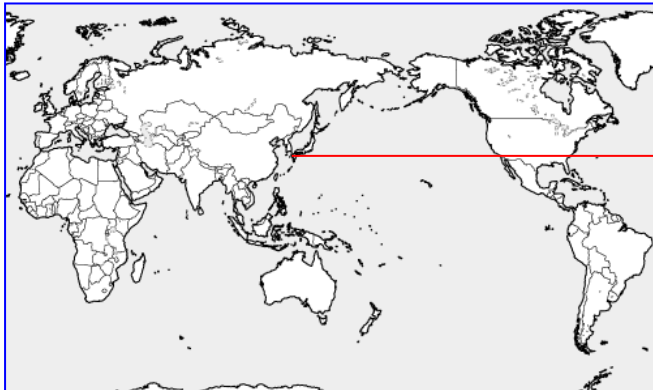
1) Introduction of OHARA Group

< OHARA INC. >

- Founded: Oct. 1, 1935**
- Locations: Chuo-ku, Sagami-hara-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 >

Innovating Technology
Together with Customers
“**Dream Fulfillment
Company**”

Electronics Business Domain

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



Optical Business Domain

- Pressings, Blocks
 - Low Tg Optical Glass
- For Digital Camera, Microscope, Telescope, etc.



High-quality advanced materials

Optical Business

Advanced molding
technology and leading-
edge materials

Electronics Business

Provide solutions through
functional materials

Environment and energy businesses

The third domain

Environmental / Energy Business Domain

- Lithium Ion Conductive
Glass-ceramics



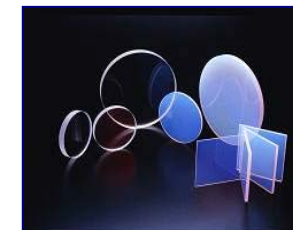
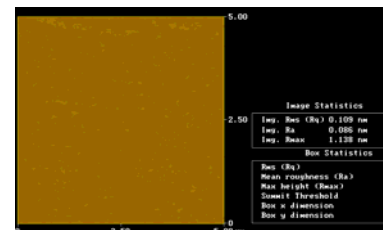
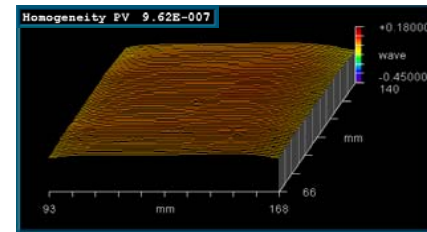
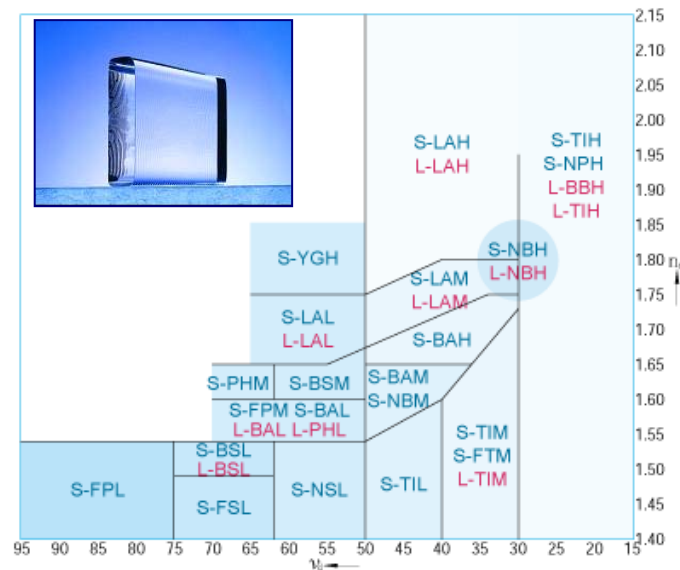
Desire to contribute to
the creating the future
for people and society

Lithium Ion Conductive Glass Ceramics (LICGC™): 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



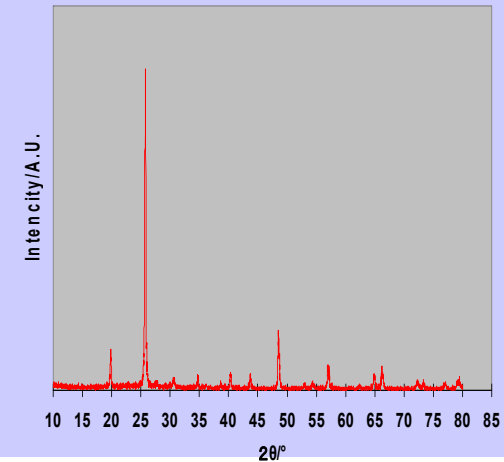
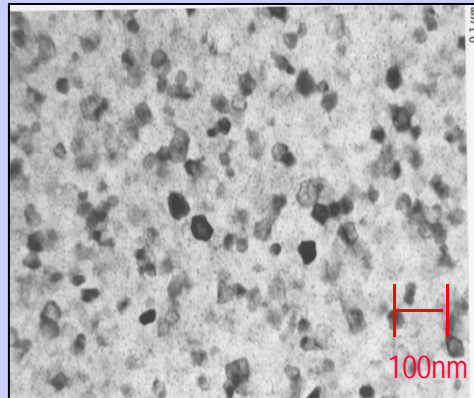
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



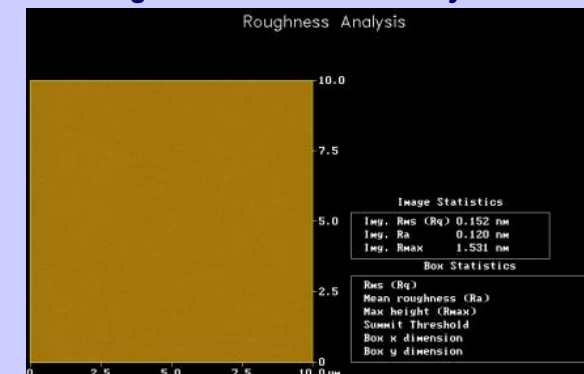
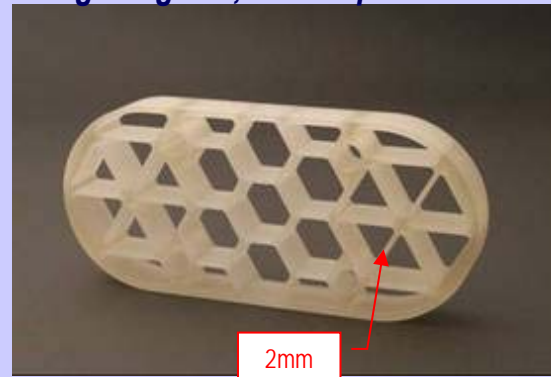
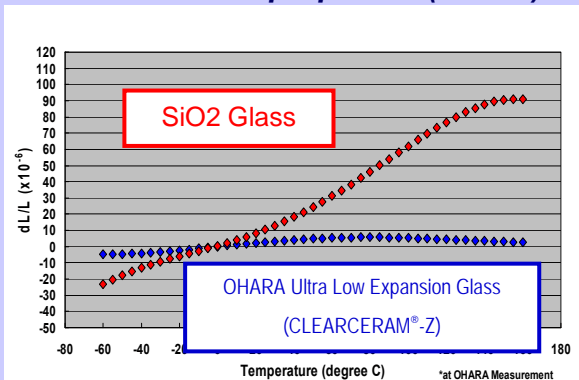
2) Technologies of OHARA Group

- Glass-ceramics Technology

- Composition / Structure: Nano-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



Symposium on Energy Storage Beyond Lithium Ion; Materials Perspective,
October 7-8, 2010 Oak Ridge National Laboratory
Kousuke Nakajima, OHARA INC.

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

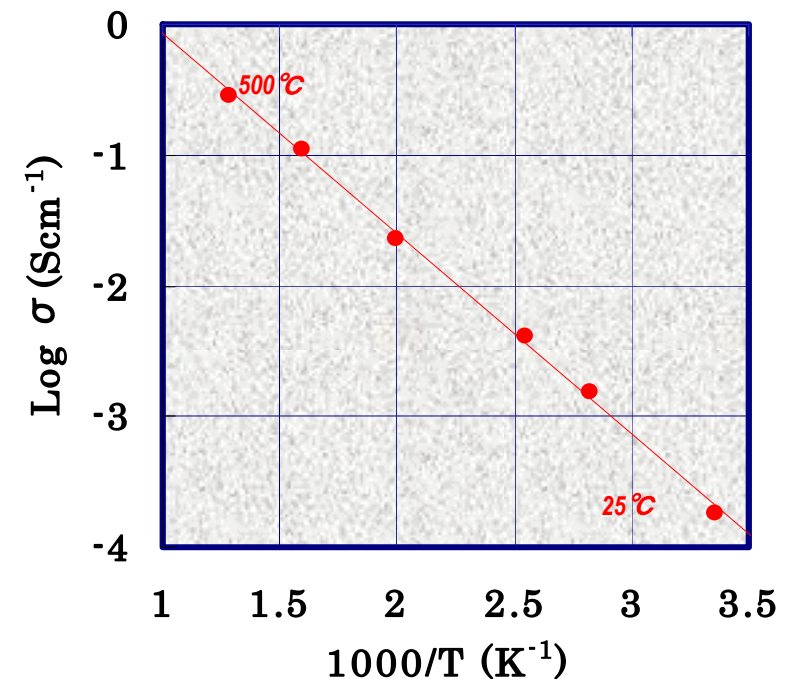
- Glass-ceramics, to have isotropically dispersed Lithium-Ion Conductive Crystal particles and an amorphous glass phase

(OHARA unique technologies, Patent Applied and Registered in JP, US and EU)

- Ohara has a US trademark on 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)



The Arrhenius plot on 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-i) Main Feature

*Presently the supply of LICGC™ 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°C
- Proved seawater stability (>2 years*)

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

b.) LICGC™ 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°C
- Scalable in terms of size & quantity

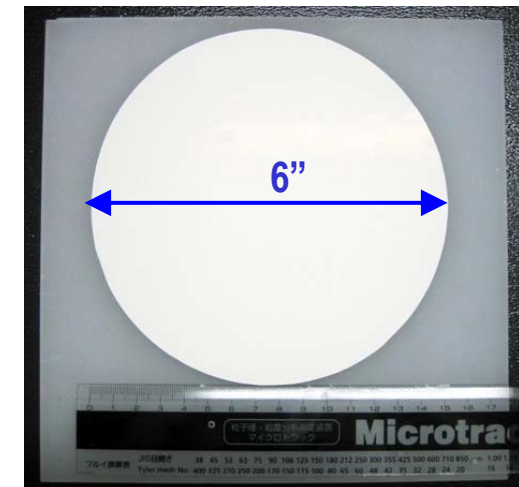
< Typical Membranes Sizes >

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



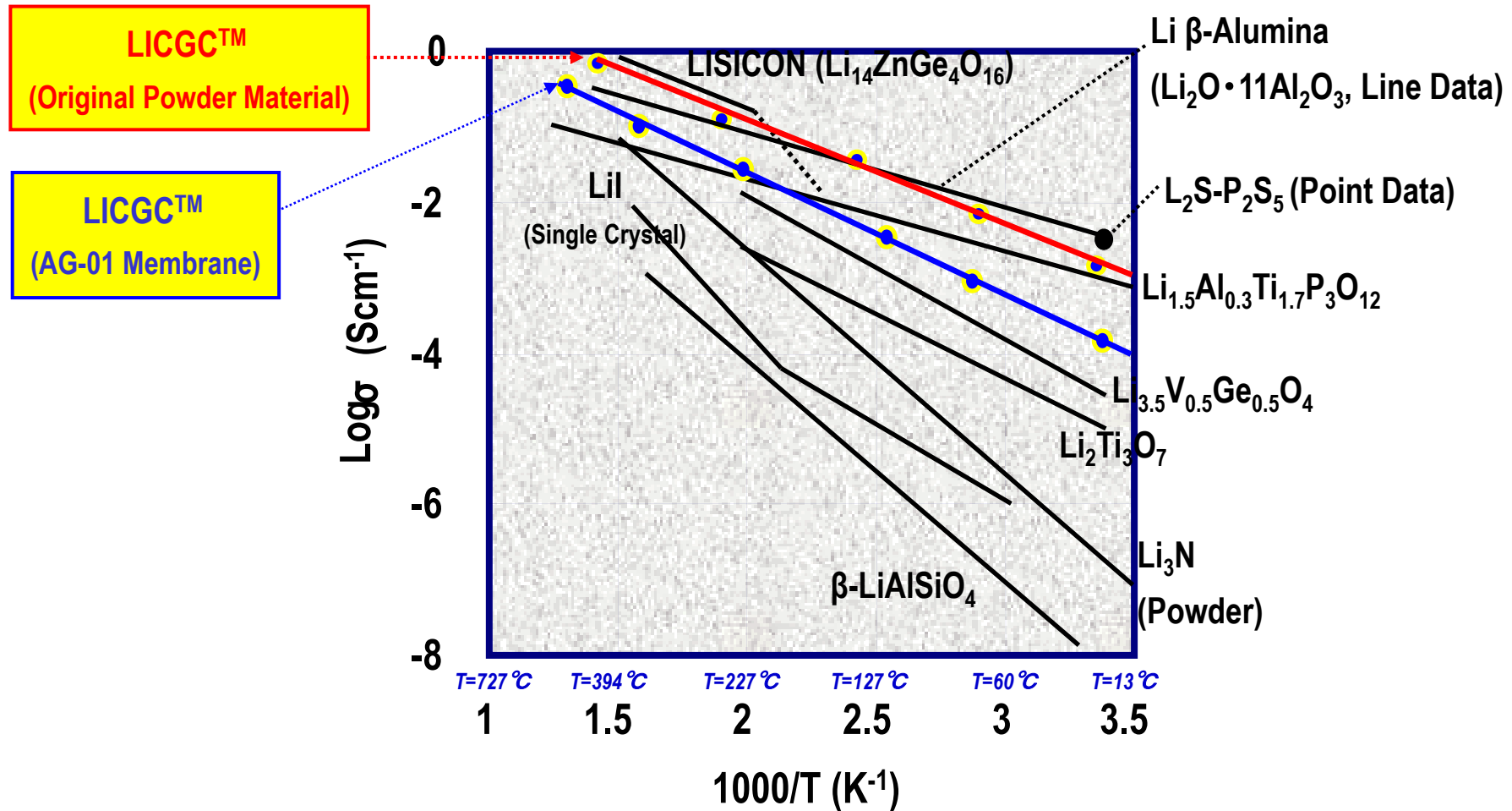
LICGC™ Tape Cast & Sintered Plate
Membrane in Dia.6"x250um thickness

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 LICGC positions in Lithium-Ion Conductive Inorganic Materials?)



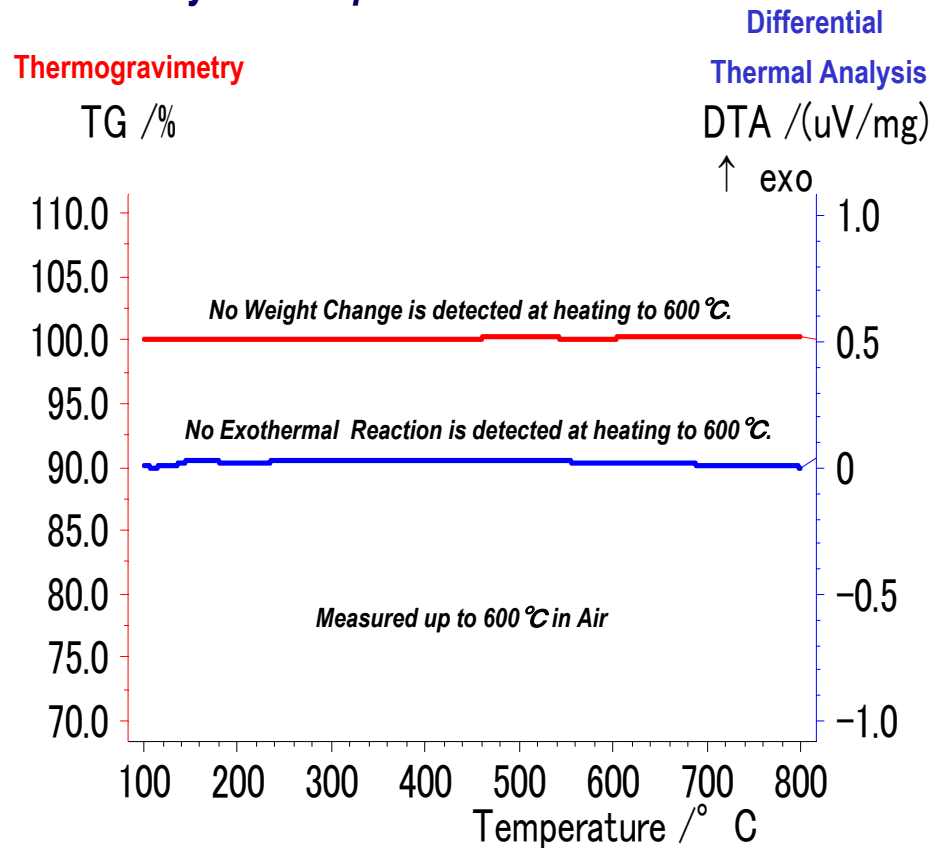
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature

Thermally Stable up to 600 °C



Nonflammable, Can be Handled in Air.



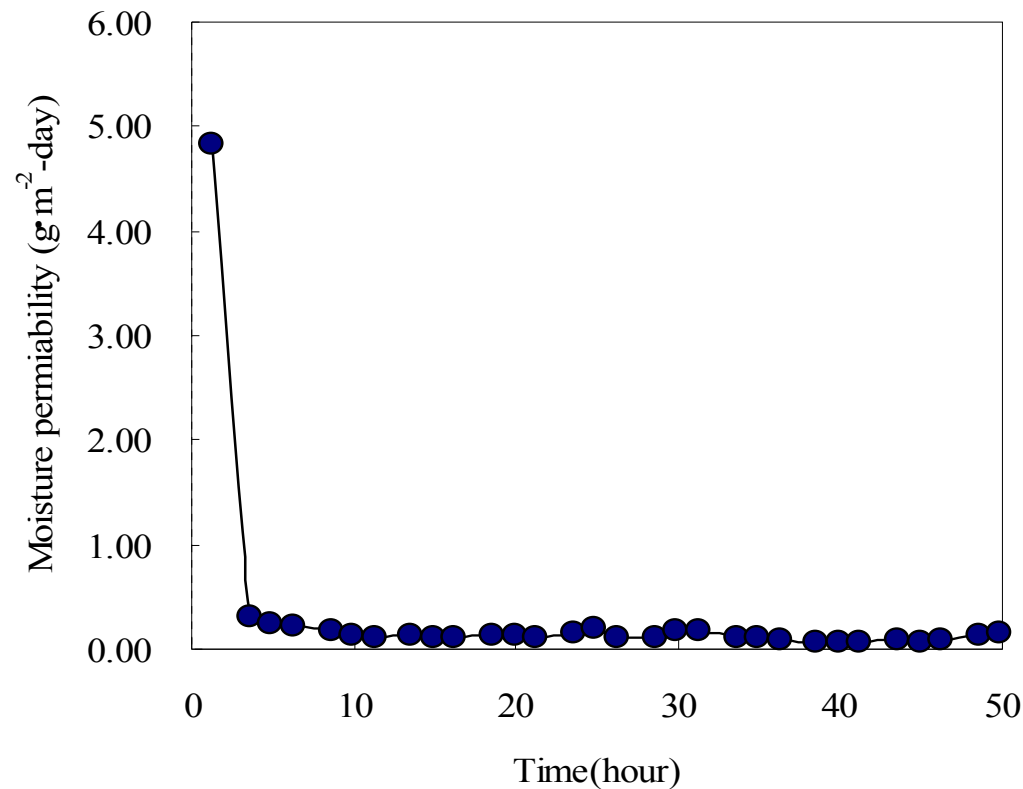
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-i) Main Feature

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



Mocon Permatran 3/33

Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-ii) General Properties (AG-01)

<i>Chemical Properties</i>	<i>Water Resistance in Powder form (RW(P) in JOGIS Class)</i>	<i>Class 1</i>
	<i>Acid Resistance in Powder form (RW(P) in JOGIS Class)</i>	<i>Class 1</i>
<i>Mechanical Properties</i>	<i>4 Point Bending Strength</i>	<i>140N/mm²</i>
	<i>Knoop Hardness (Hk)</i>	<i>590</i>
	<i>Specific Gravity</i>	<i>3.05</i>
<i>Thermal Properties</i>	<i>Coefficient of Thermal Expansion</i>	<i>94 x 10⁻⁷/degree C (30 ~ 350degree C)</i>
		<i>82 x 10⁻⁷/degree C (350 ~ 600degree C)</i>

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

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

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

Sub Crystal Phase: $AlPO_4$

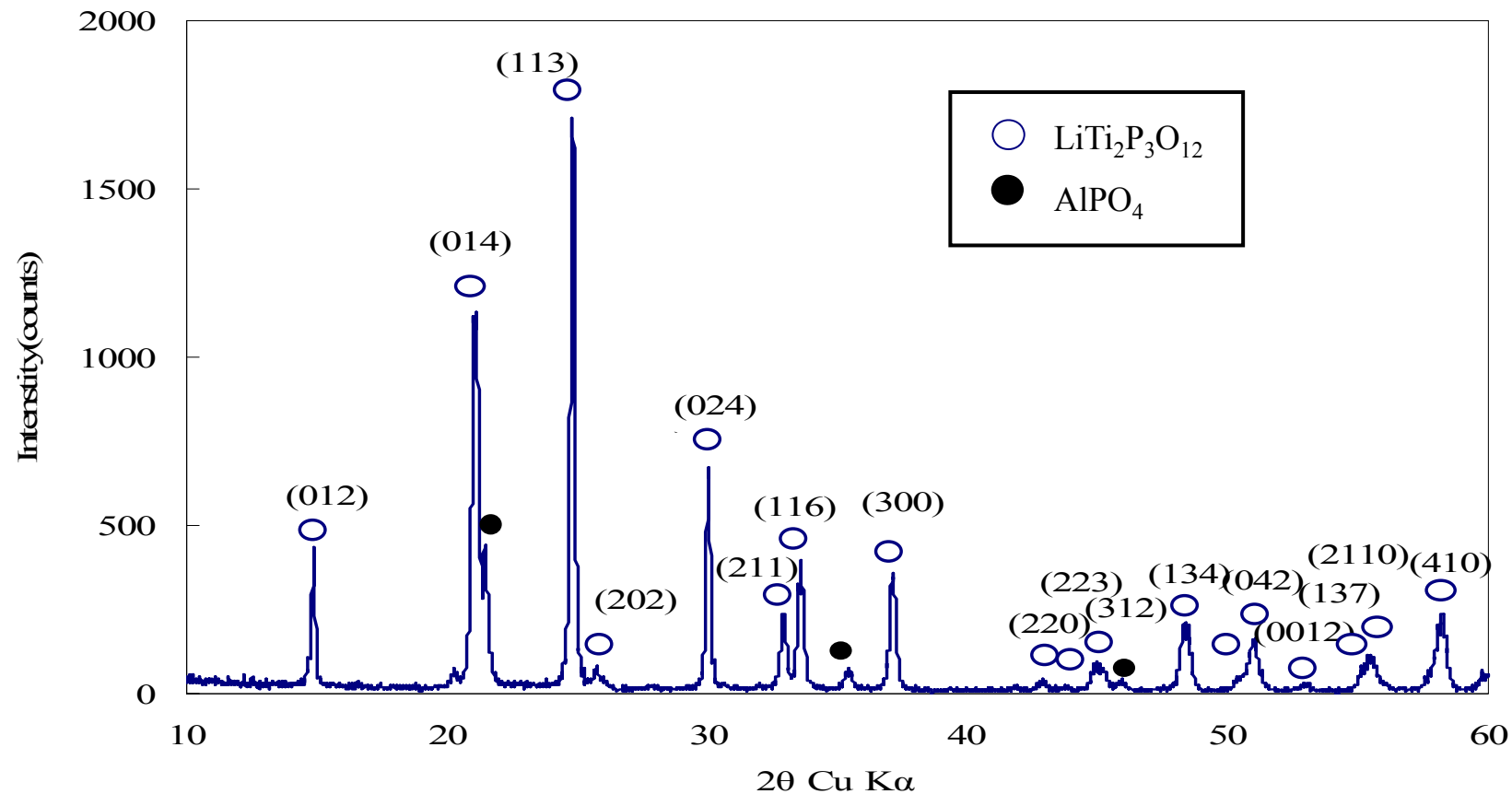
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

- X-Ray Diffraction



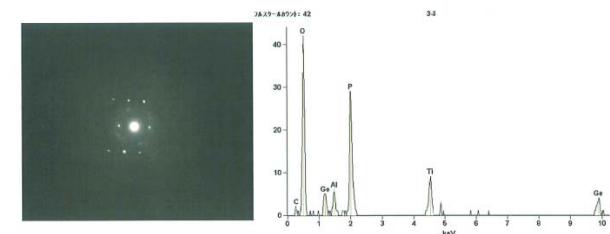
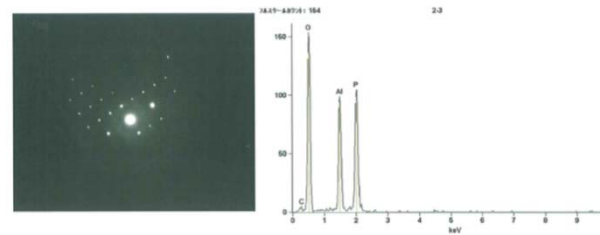
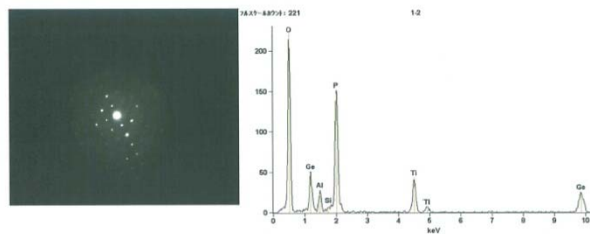
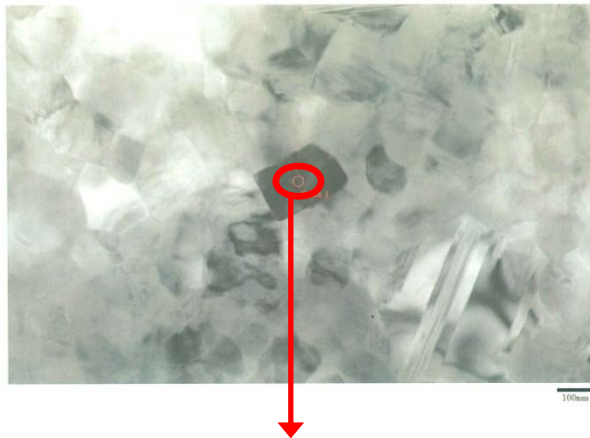
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

- TEM & EDX



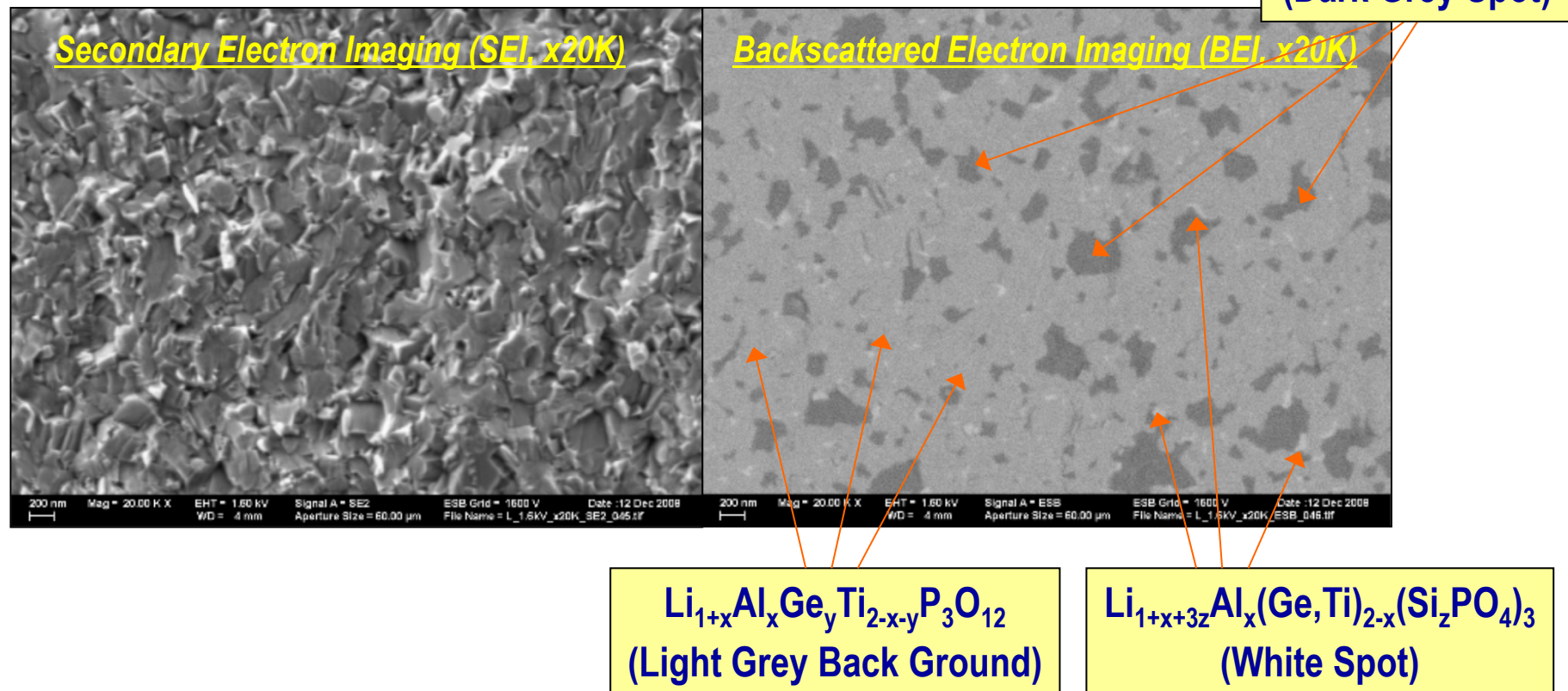
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



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

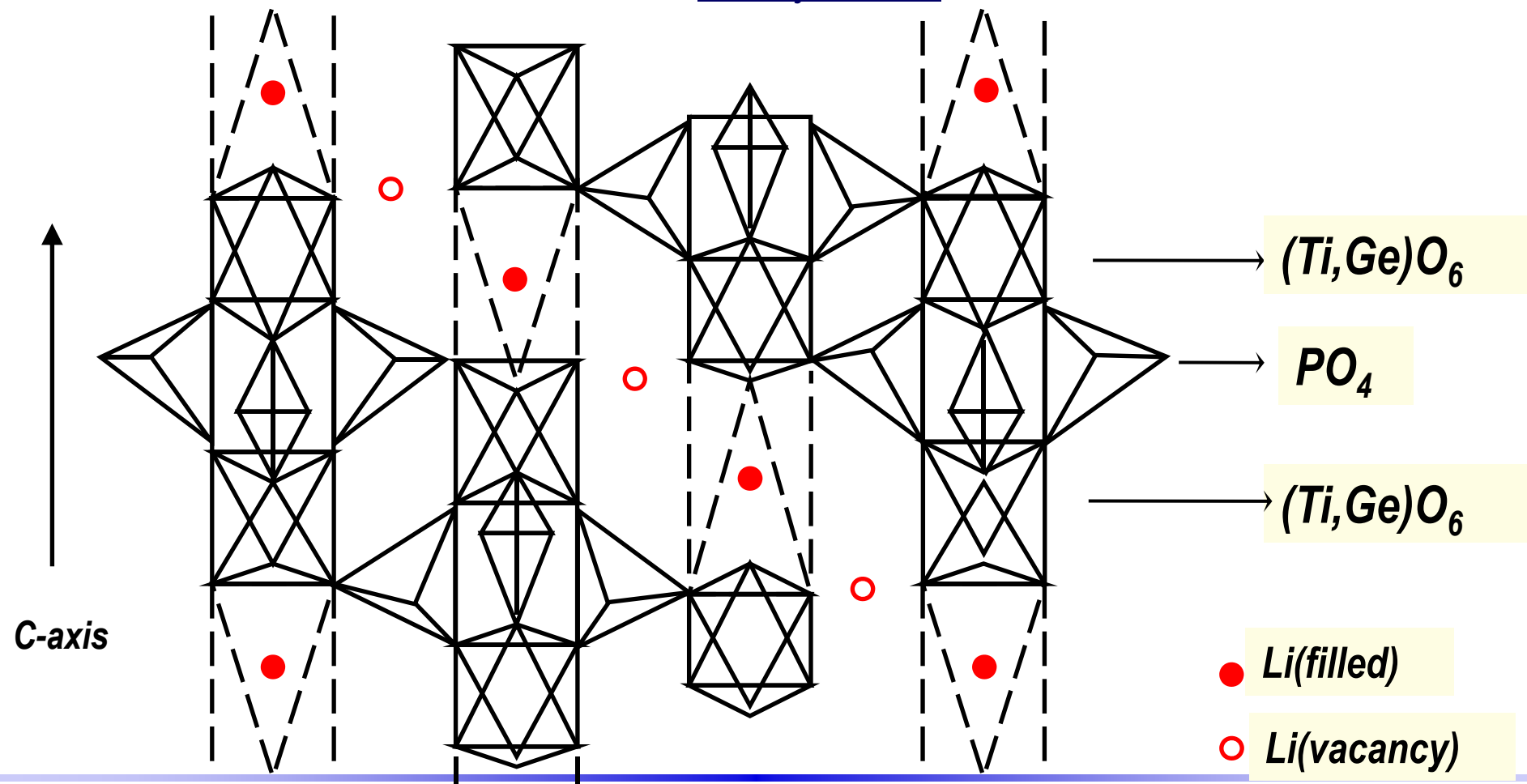


Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

- Li Ion Conduction Mechanism in the material: Vacancy Diffusion



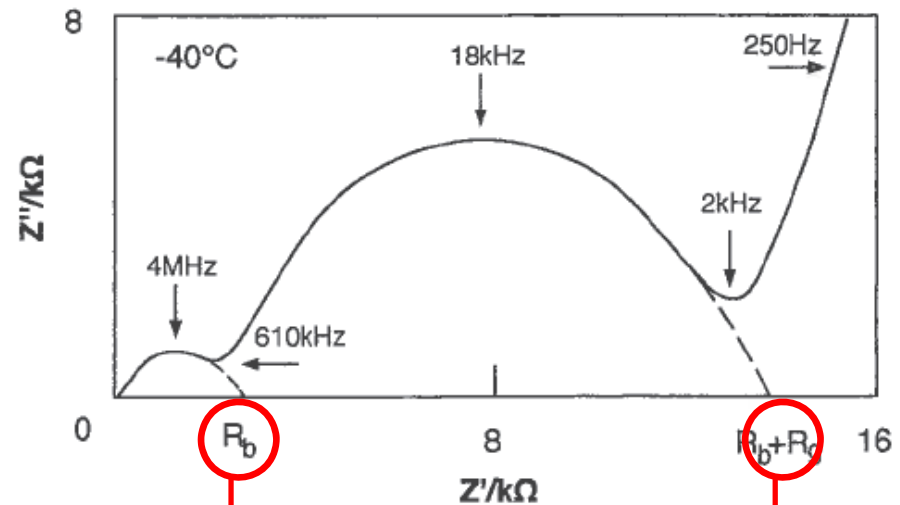
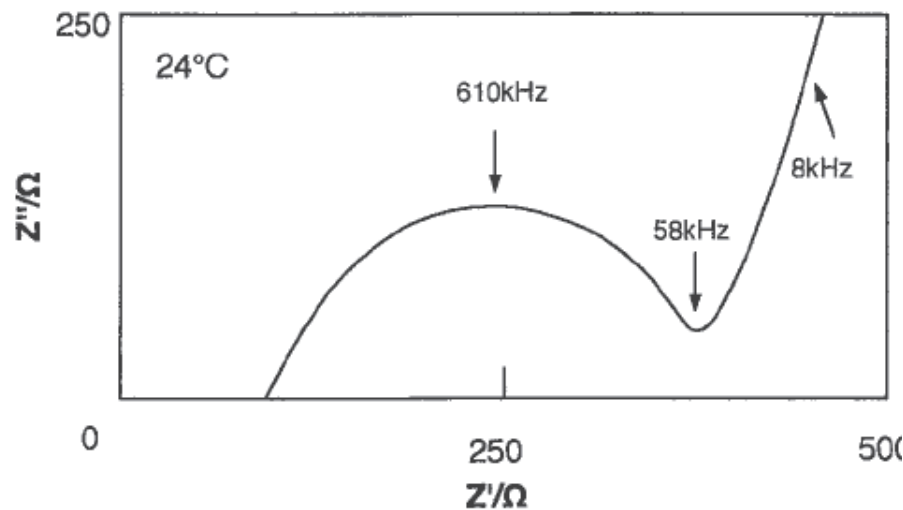
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

3-iii) Composition & Structure

Complex Impedance plot for LICGC™ (Original Powder Material)



R_b : Attributed to
“Bulk of Grain”

R_g : Attributed to
“Grain Boundary”

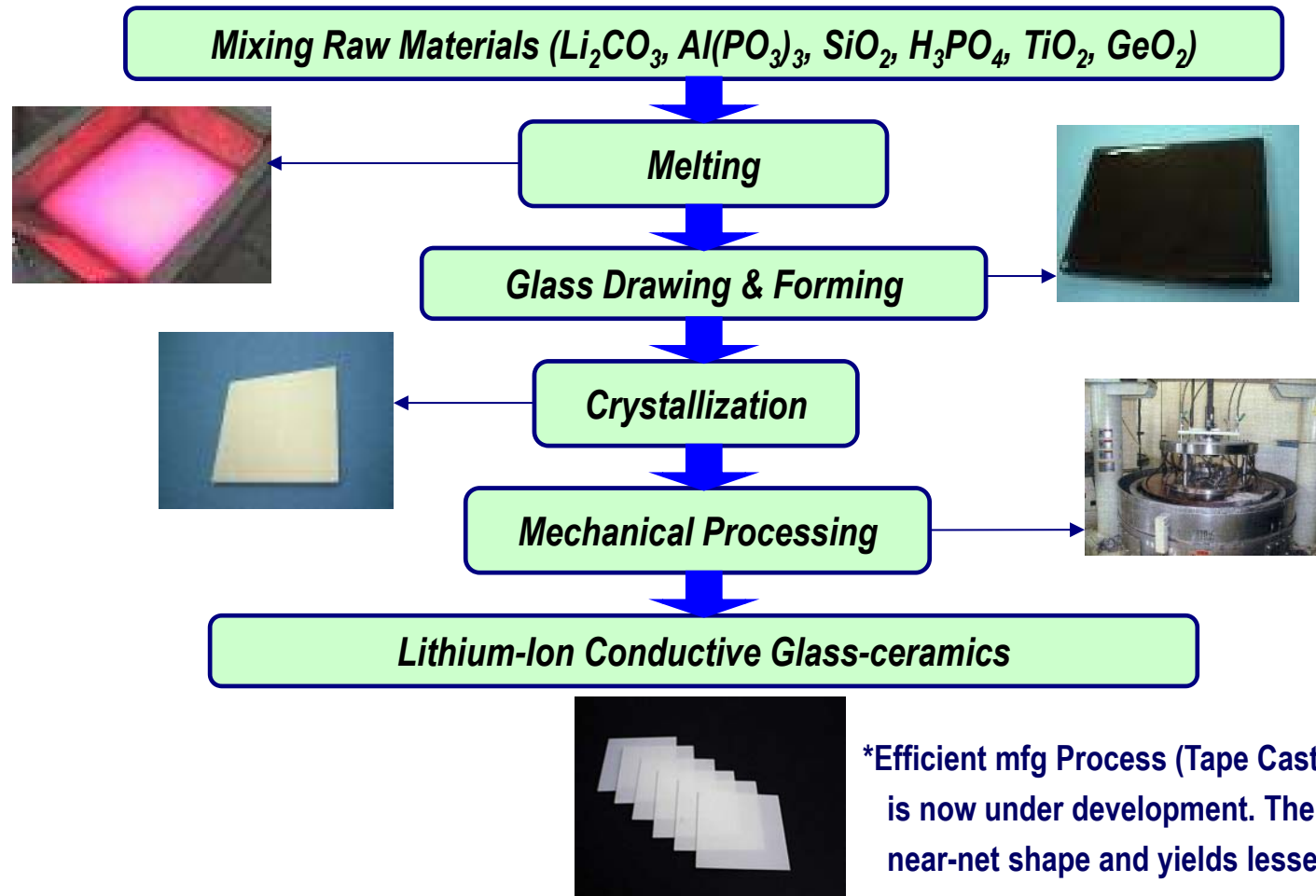
J. Fu, J. Am. Ceram. Soc., 80 (1997) 903-1901

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)



Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

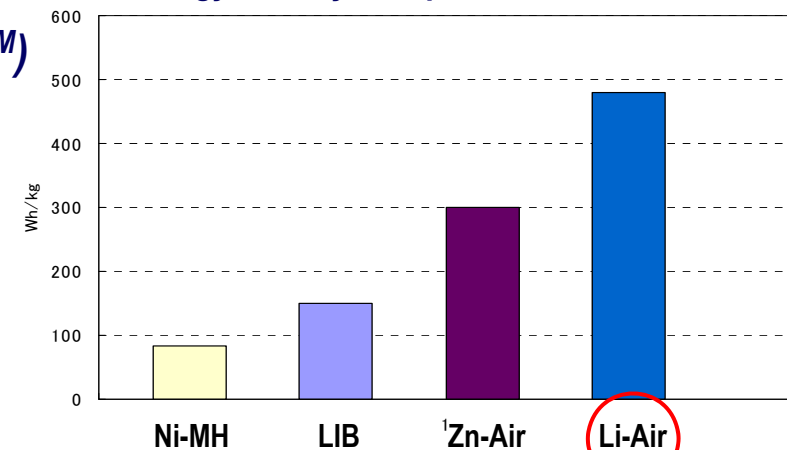


3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

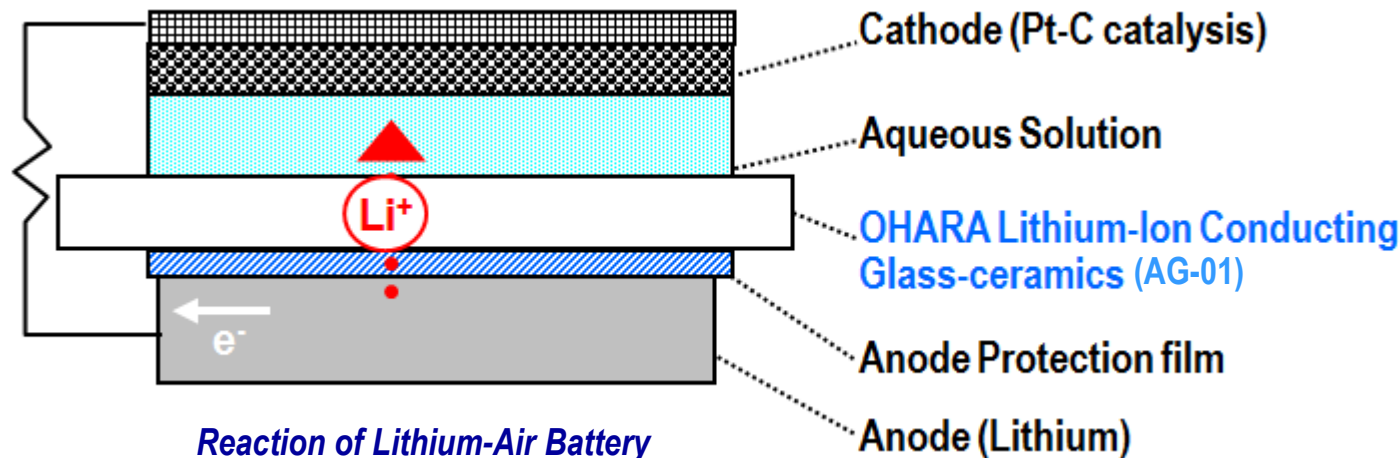
3-v) Application

(Solid Electrolyte for **Elemental Li / Air Battery**)

Energy Density Comparison



Li / Air Cell Structure



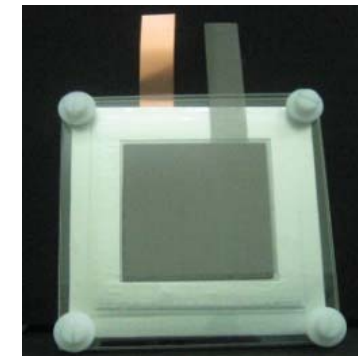
Reaction of Lithium-Air Battery

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

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

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

Li / Air Prototype Cell
for solid electrolyte
evaluation
(Using Sq.2" LICGC™ AG-01)



Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

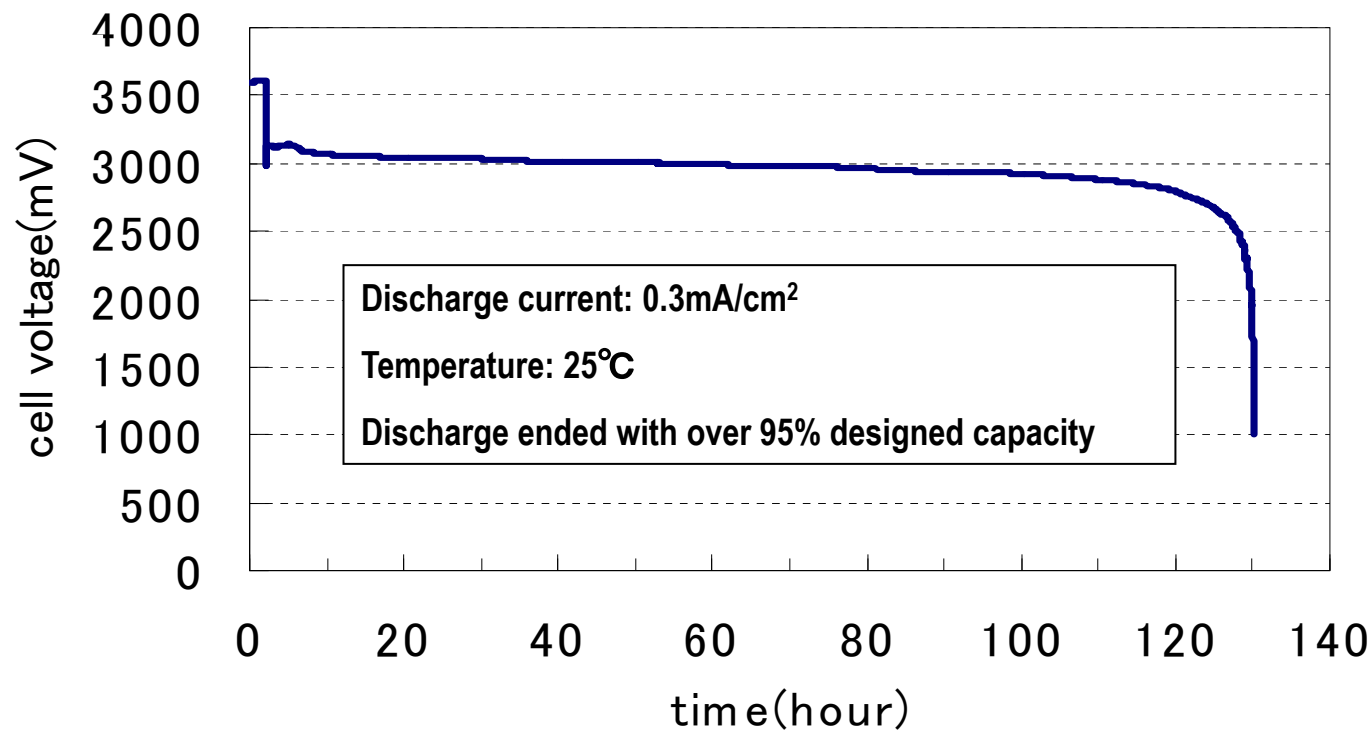


3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

Li / Air Cell Performance

Discharge curve for the Demonstrative Primary Li / Air Cell



Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries

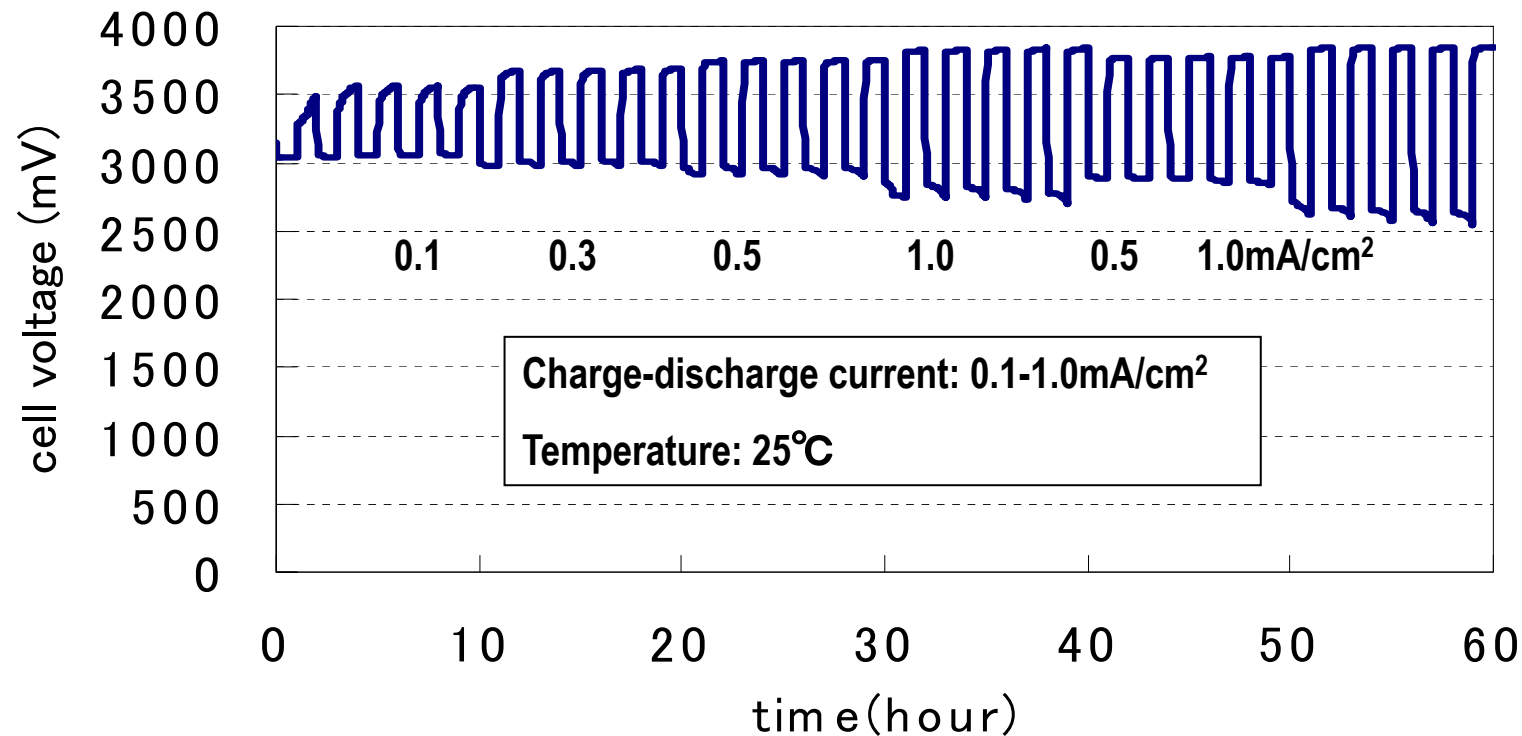


3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

Li / Air Cell Performance

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



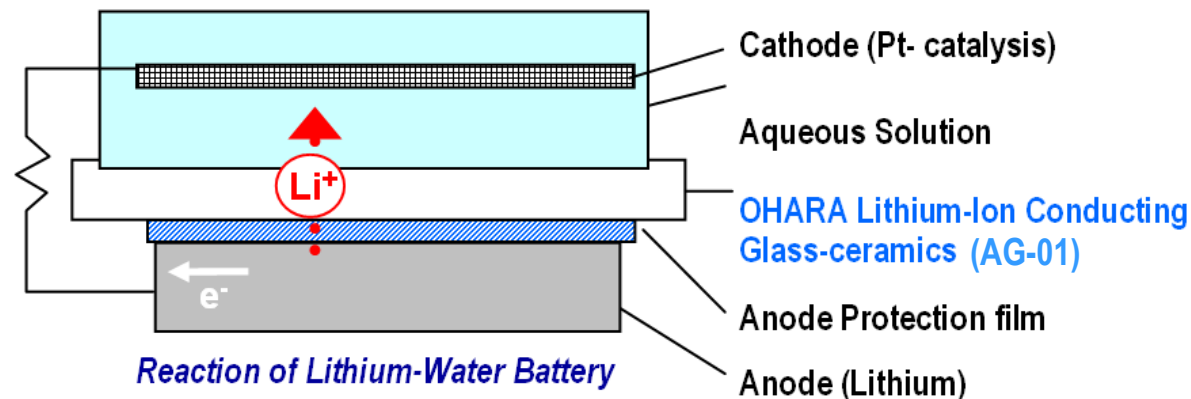
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



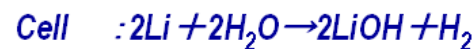
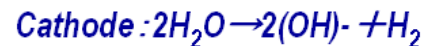
3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

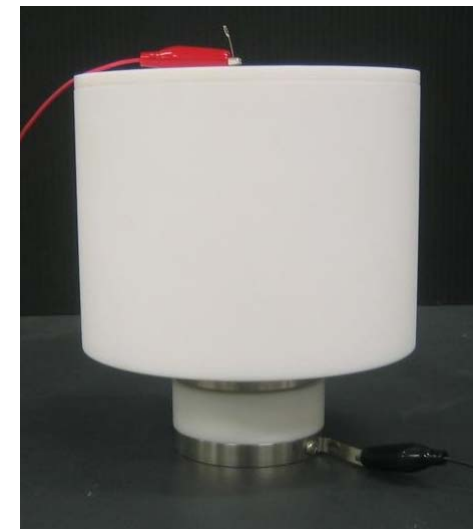
Li / Seawater Cell Structure



Reaction of Lithium-Water Battery



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



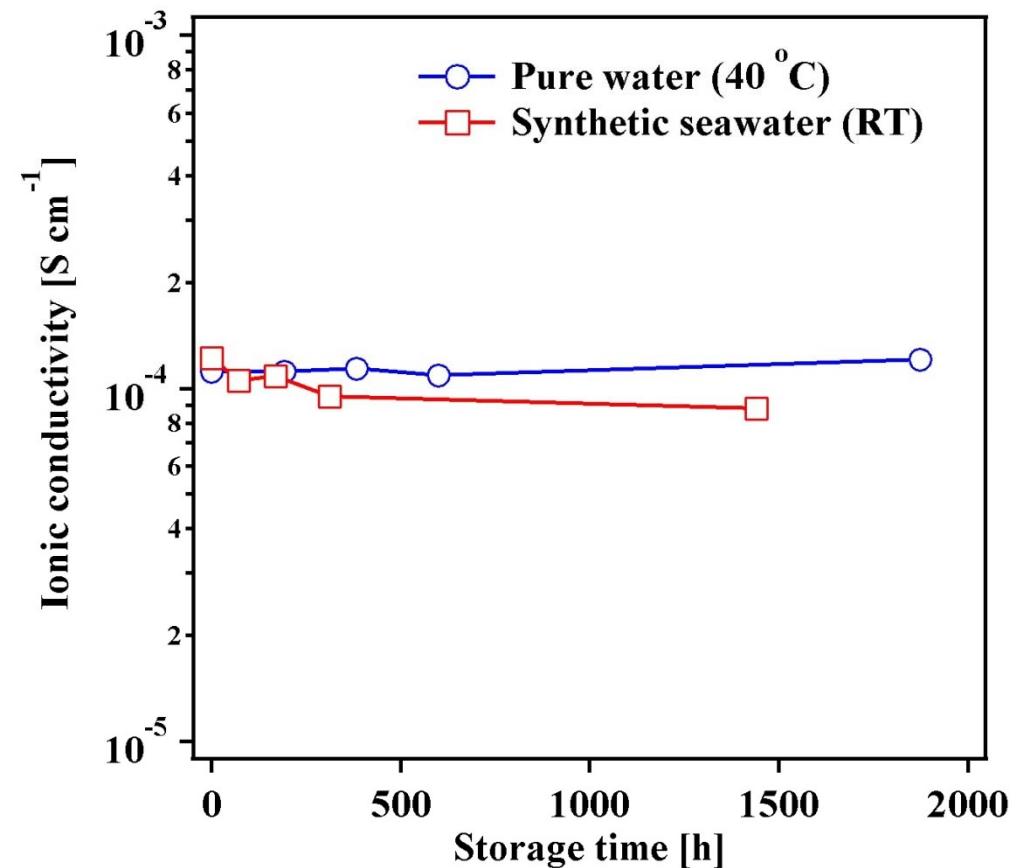
Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

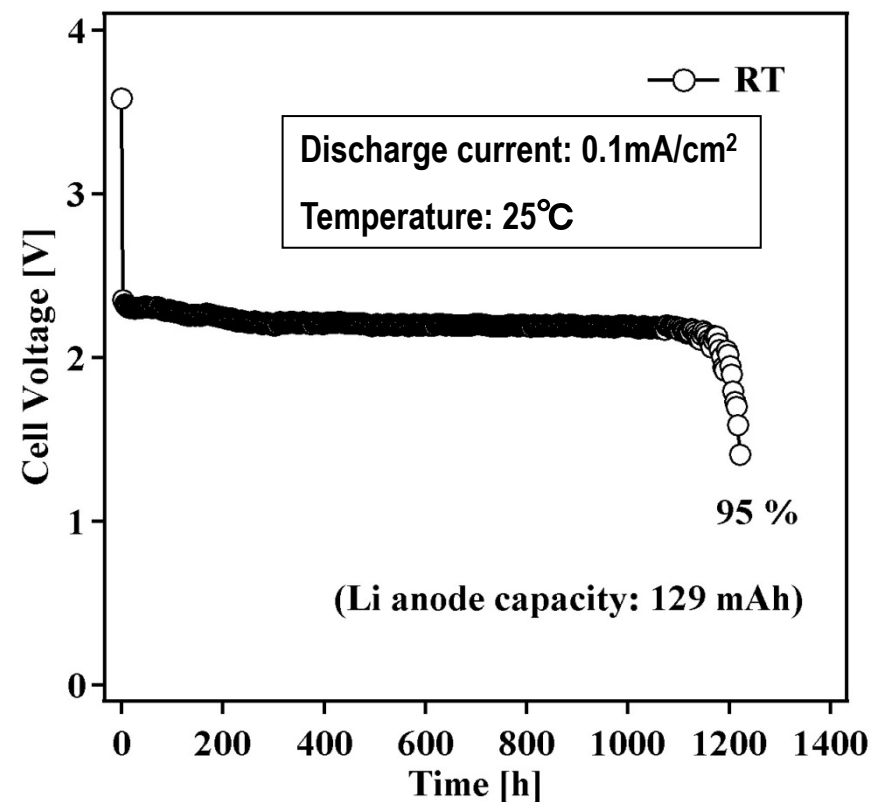


3) The Lithium Ion Conductive Glass Ceramics (LICGC™)

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

Li / Seawater Cell Performance

Discharge curve for the Demonstrative Primary Li/Seawater Cell



Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal Batteries



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.***

Lithium Ion Conductive Glass Ceramics (LICGC™): Properties and Application in Lithium Metal 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.