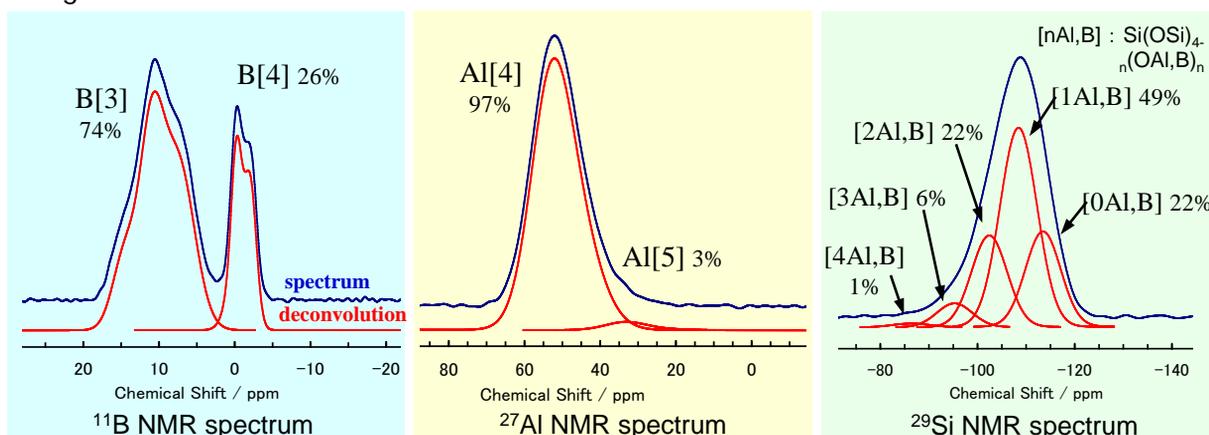


Analyzing inorganic materials.

Many of inorganic materials like glasses and zeolites consist of elements, such as Si, Al, and B. With the solid-state NMR, it is able to acquire the information of neighboring structure combined to Si and information of the coordination number about Al and B.

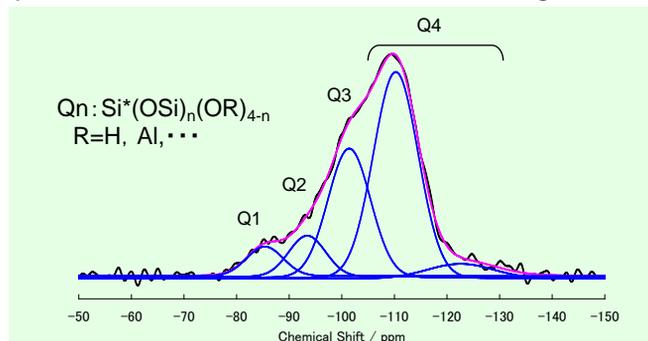
Chemical structure of alumino-borosilicate glass

In order to perform structural analyses of the alumino-borosilicate glass, ^{11}B , ^{27}Al , and ^{29}Si NMR measurements were carried out. It was possible to estimate the composition ratios of the components for the different coordination number around Al and B, and for the various neighbor structure around Si.



Si / Al ratio of zeolite

To determine the Si / Al ratio in the framework of a zeolite sample, ^{29}Si NMR measurement was performed. The composition ratio calculated by the deconvolution of spectrum was summarized at the following table.



Q1	Q2	Q3	Q4	Si/Al	$\text{SiO}_2/\text{Al}_2\text{O}_3$
5.9%	8.3%	29.9%	55.9%	6.2	12.4

Many of elements in inorganic materials are quadrupolar nuclei. So the line shapes tend to be distorted and broadened due to the nuclear quadrupole interaction in these solid-state NMR spectra. For Al and B, it is possible to suppress the coordination number by using a high magnetic field NMR apparatus.

NMR measurable oxygen isotope is only ^{17}O nucleus, of which natural abundance ratio is mere 0.04%. Therefore, although inorganic materials like glass or zeolite include many oxygen, it is impossible to measure except for ^{17}O labeled samples.

Evaluating lithium ion battery.

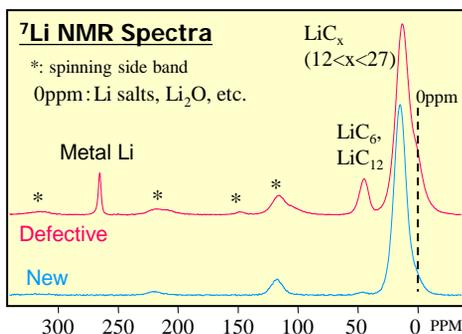
The chemical state information in the anode and cathode of lithium ion battery (LIB) can be obtained quantitatively by solid-state NMR. The sampling in the inert atmosphere enables the analysis without the damage caused by the atmospheric air and moisture exposure of samples.

Chemical state of lithium in anodes

To investigate the degradation of the anode active material in LIB, solid-state ^7Li NMR measurements were carried out the two samples.

From ^7Li NMR spectra, the abundance ratio of each component was estimated.

In the defective, metal Li was detected, and lithium salts or lithium oxide were increased.



sample	Metal Li	$\text{LiC}_6, \text{LiC}_{12}$	LiC_x ($12 < x < 27$)	Li salts Li_2O , etc.
New	—	1 mol%	88 mol%	11 mol%
Defective	3 mol%	8 mol%	66 mol%	23 mol%

Since Li amount in a sample can quantity by the ICP-AES method, it is also useful to combine with the results of solid-state NMR.

Li element has another NMR observable isotope ^6Li . The advantage of ^6Li is the smaller effect of quadrupole interaction than ^7Li .

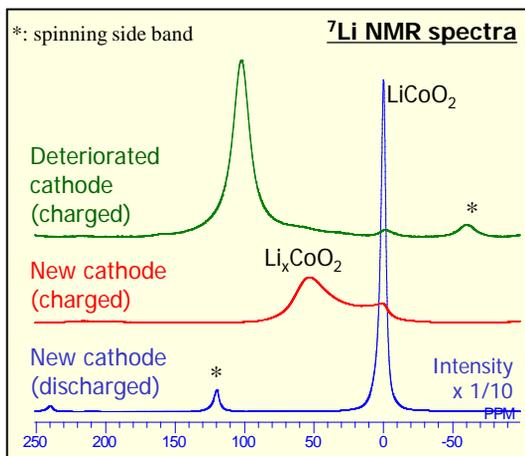
Although natural abundance ratio of ^6Li is as low as 7.6% and then the sensitivity is very low, it is possible to take full advantage of ^6Li with usage of ^6Li enrich samples

Chemical state of lithium in cathodes

For the cathode of LIB (mixture of LiCoO_2 and $\text{Li}(\text{Co},\text{Ni},\text{Mn})\text{O}_2$), in order to assess the difference in chemical states of Li between three conditions, ^7Li NMR measurements are performed. The larger chemical shift of Li_xCoO_2 ($x < 1$) for the deteriorated cathode in charged state indicates that Li is in fewer states ($x \ll 1$) and the charge-discharge efficiency was fallen.

However, the signal of $\text{Li}(\text{Co},\text{Ni},\text{Mn})\text{O}_2$ containing paramagnetic Ni and Mn was difficult to detect in this measurement condition.

sample	LiCoO_2
New discharged	LiCoO_2 peak appears about 0 ppm.
New charged	Li_xCoO_2 ($x < 1$) is present and its peak appears about 50 ppm.
Deteriorated charged	Li_xCoO_2 ($x < 1$) is present and its peak appears about 100 ppm.

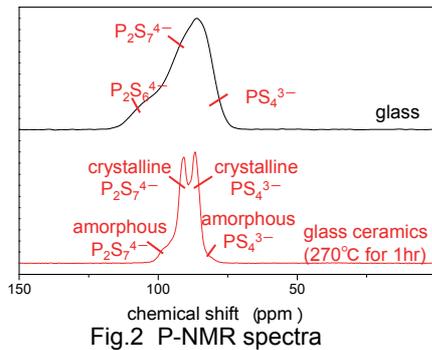
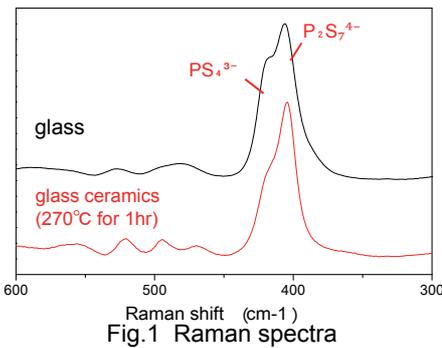


Structural analysis of sulfide solid-state electrolytes - Next-generation battery material -

Heating of sulfide solid electrolyte results in the changes of its chemical structure, crystallinity and Li ion mobility. Raman, Solid-state NMR, Outgas analysis and XRD provide these information and are useful for developing new solid electrolytes and evaluating their performance.

Sample: $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ ($\text{Li}_2\text{S} : \text{P}_2\text{S}_5 = 70 : 30$) supplied by Dr. Tabuchi, AIST Kansai

Structural change by heat treatment



	Relaxation time T_1 (s) of ^7Li
Glass	11.2
Glass ceramics	3.7

Table 1. Relaxation time of ^7Li (by NMR)

- Change in Raman and P-NMR spectral shapes => Increase in crystallinity by heat treatment
- Decrease in T_1 of lithium => Increase in mobility of Li ions

It is crucial to know changes in chemical and crystalline structures with heat treatment for understanding the relation between ion conductivity and chemical structures.

Structural change during heat treatment

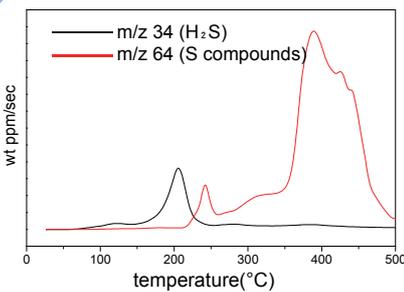


Fig.3 Outgas with rising temperature

Outgas and Raman spectral change during heating:

- Outgas analysis showed that sulfur was generated above 200°C.
 - Raman analysis also showed a band of sulfur.
- => Sulfur desorption started at about 200°C in the heat treatment process.

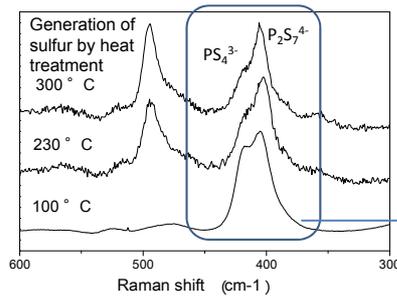


Fig.4 Raman spectral change with rising temperature

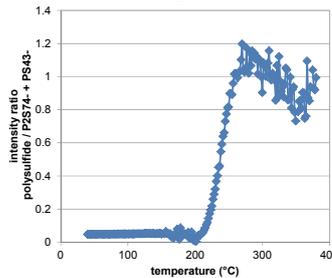


Fig.5 Relative intensity of polysulfide against $\text{P}_2\text{S}_7^{4-}$ and PS_4^{3-}

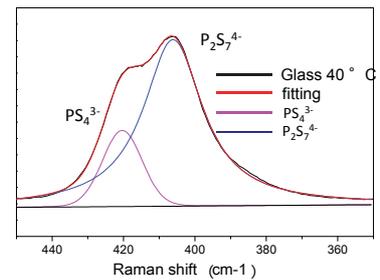


Fig.6 Peak separation of Raman bands

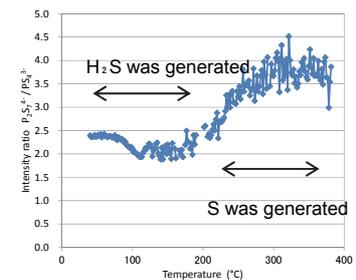


Fig.7 Relative intensity of $\text{P}_2\text{S}_7^{4-} / \text{PS}_4^{3-}$

- Change in Intensity ratio of $\text{P}_2\text{S}_7^{4-} / \text{PS}_4^{3-}$ => Content ratio of $\text{P}_2\text{S}_7^{4-}$ slightly tended to decrease under 200°C. Content ratio of PS_4^{3-} decreased above 200°C.

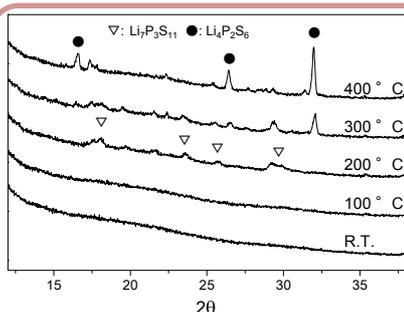


Fig.8 XRD profile change

High temperature in situ XRD measurements

- $\text{Li}_7\text{P}_3\text{S}_{11}$ component started crystallization about 200°C.
 - $\text{Li}_4\text{P}_2\text{S}_6$ component started crystallization about 400°C.
- => Change in the structure of $\text{P}_2\text{S}_7^{4-}$, generation of structure of $\text{P}_2\text{S}_6^{4-}$ and its progress in crystallization with rising temperature were suggested.

- Structural analysis such as NMR, Raman and XRD
- Outgas analysis

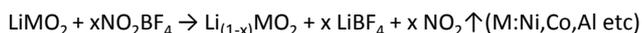
- => reveal chemical structural changes and crystallization behavior induced by heat treatment,
- => useful for optimizing preparation conditions of solid electrolyte and examining possible correlation between those changes and ion conductivity.

Structural analysis of LIB cathode material using Chemical Delithiation/Lithiation

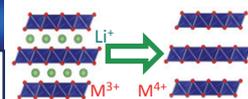
We can prepare model active materials of various SOC alone by chemical delithiation / lithiation, without influence from the other components in an actual cell. It enables us to examine their thermal stability, crystal structure and local environment around Li ions at various charging / discharging states.

【Example : NCA(LiNi_{0.8}Co_{0.15}Al_{0.05}O₂)】

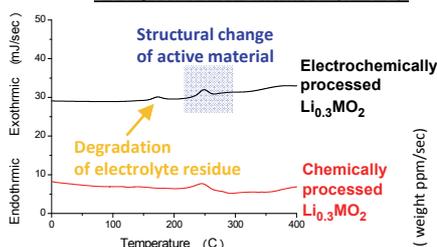
【Charged model samples: Chemical Delithiation】 to simulate / evaluate various SOC-cathodes



LiMO₂ is delithiated by oxidant.

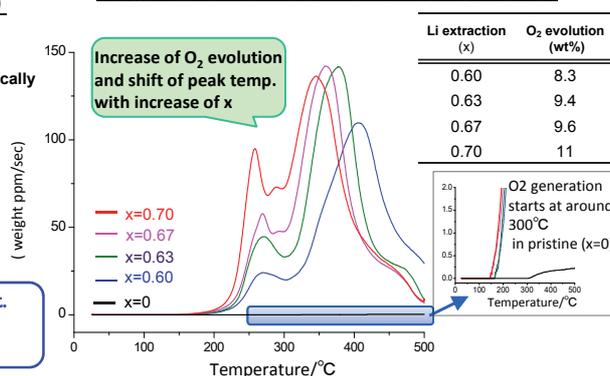


DSC profiles of Li_{0.3}MO₂ (x=0.7)

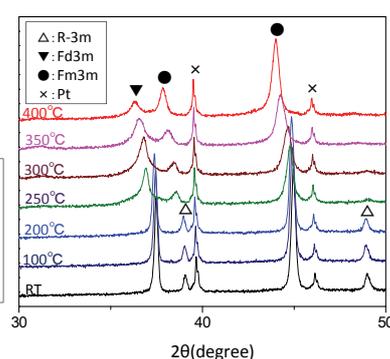


Exothermal behaviors are slightly different.
⇒ Influence from the other components should be eliminated.

Oxygen generation rate of Li_(1-x)MO₂ by TPD-MS

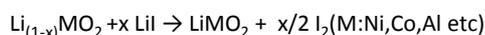


HT-XRD patterns of Li_{0.3}MO₂ (x=0.7)

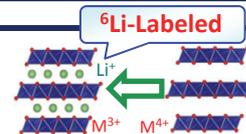


✓ Chemical Delithiation enables us to evaluate thermal stability/crystal structure without influence of other components.

【Discharged model samples: Chemical Lithiation】 to reveal inserted Li sites

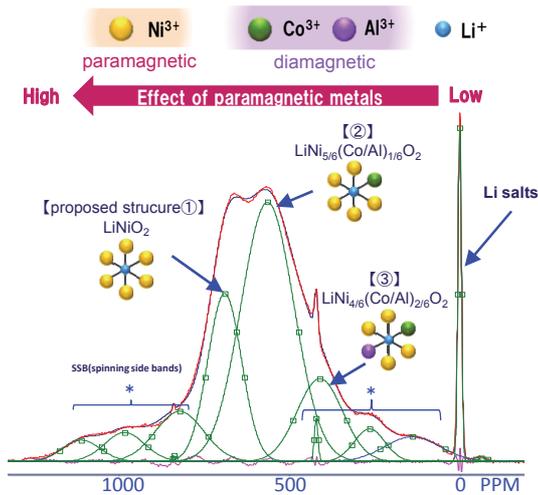


Li_(1-x)MO₂ is lithiated by reductant.



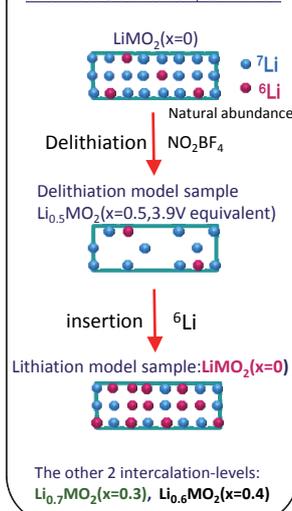
-Local structural analysis around Li ion by solid-state NMR-

⁷Li MAS NMR spectrum of LiMO₂ (x=0)



Chemical shifts are influenced by paramagnetic metals around Li.
(Ref.: Journal of The Electrochemical Society, 162 (7), A1315-A1318 (2015))

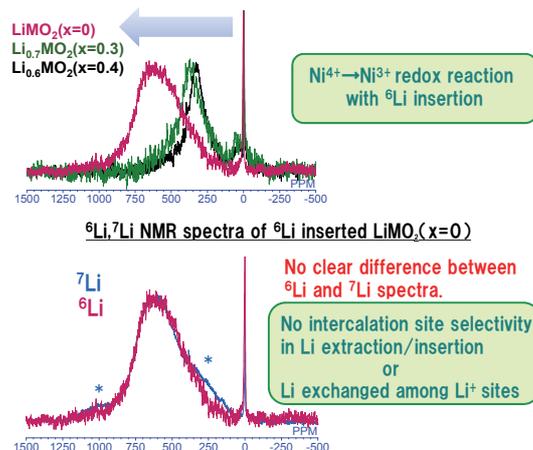
Chemical Delithiation/Lithiation



The other 2 intercalation-levels:
Li_{0.7}MO₂(x=0.3), Li_{0.6}MO₂(x=0.4)

⁶Li, ⁷Li MAS NMR spectra of Chemical Lithiated samples

⁶Li NMR spectra at various ⁶Li inserting states



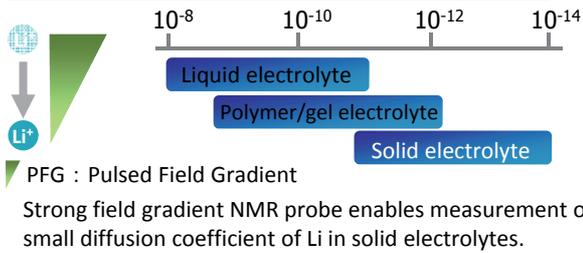
✓ Chemical Lithiation enables us to analyze local structural change around Li ion in ⁶Li-labeled cathode materials.

Chemical Delithiation/Lithiation is useful for analyzing charge-discharge reaction in cathodes and designing materials.

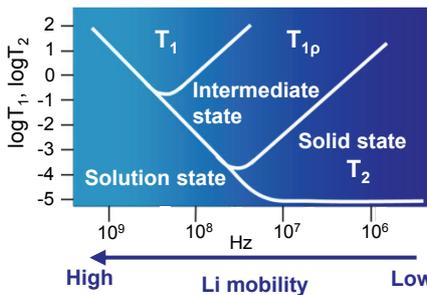
Li ion dynamics measurement and in situ Li depth profiling of solid state electrolyte

Our services of diffusion coefficient and relaxation time analysis by NMR is useful for Li mobility evaluation. Also we provide in situ NRA analysis for depth profiling of Li around electrode/solid electrolyte interface at controlled voltages along with electrochemical data.

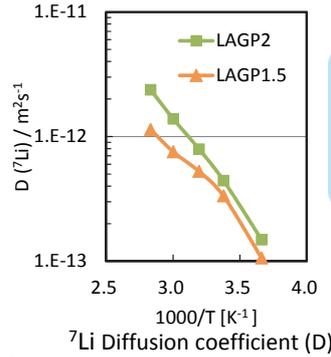
Diffusion coefficient and Relaxation time measured by NMR



Diffusion coefficient $D \rightarrow$ Translational Li diffusion
Relaxation times $T_1, T_{1\rho}, T_2 \rightarrow$ Local Li mobility

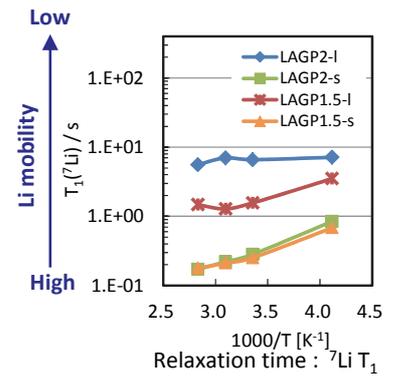
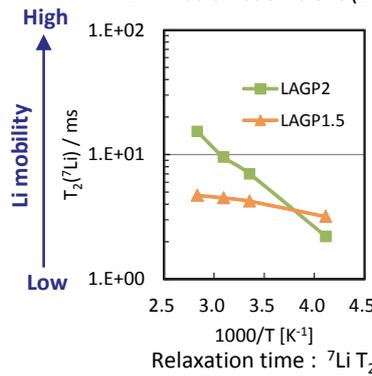


● Samples : LAGP Solid electrolytes



- Temperature dependence of diffusion coefficient D and relaxation time T_2 of ^7Li
 \rightarrow Li in LAGP 2 showed higher mobility
- Relaxation time T_1
 \rightarrow Possible existence of low mobility Li

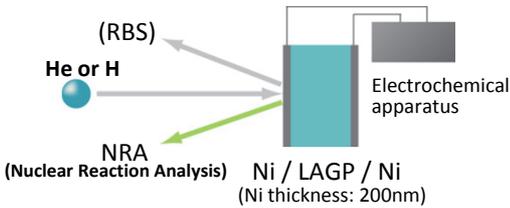
Valuable for wide range Li mobility evaluation



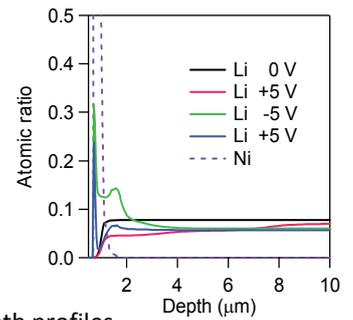
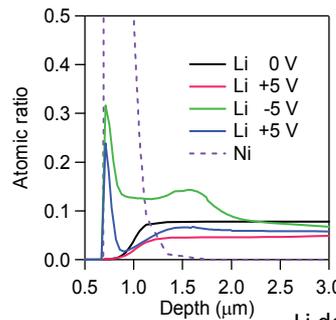
Li distribution under applied voltage measured by *in situ* NRA

● Sample: Ni / LAGP 1.5 / Ni

(Ni was chosen as electrodes for its low absorbance of Li.)

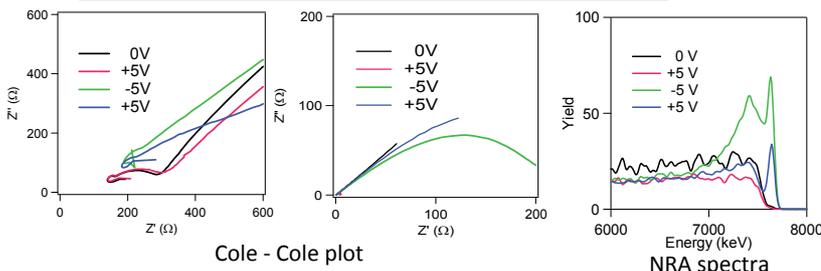


Sample is introduced into analysis chamber under inert atmosphere. After electrochemical measurements, Li depth distribution is measured at controlled voltage.



Li depth profiles

- 0V \rightarrow +5V : Increase in bulk resistivity
 \Leftrightarrow Li depletion under Ni/LAGP interface
- +5V \rightarrow -5V : large arc in Cole-Cole plot
 \Leftrightarrow Segregation of Li to Ni surface, Li rich layer formation under Ni/ LAGP interface
- -5V \rightarrow +5V : large arc in Cole-Cole plot
 \Leftrightarrow Remain of segregated Ni at surface

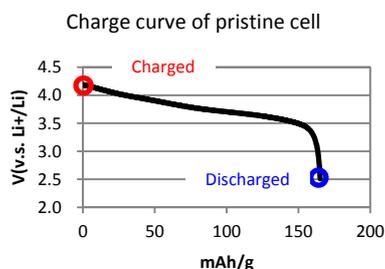


Li depth profiling at controlled voltages is beneficial for appropriate interpretation of electrochemical behavior.

XAFS and STEM analysis of high resistance phase increased in NCA cathode of LIB III-1

To clarify degradation mechanism in cathode active materials under various test conditions, we provide analysis services of surface valence state, local valence state and crystal structure distribution in active materials of test cells at controlled states of charge.

Samples



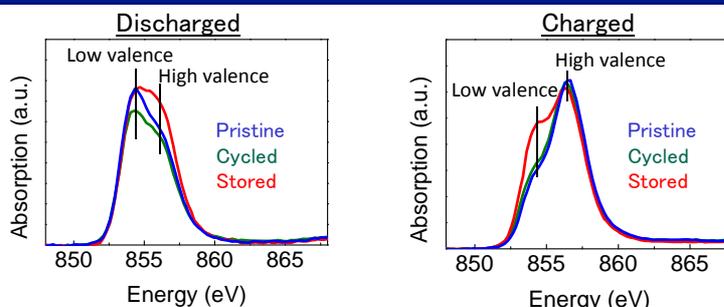
Laminate cells (1100 mAh)

- Cathode: $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA)
- Anode: graphite
- Electrolyte: 1M LiPF_6 + EC/DEC (3/7) + VC

1. Pristine (Electrochemically activated)
2. Cycle-tested (0.5C x 200cycles at RT)
3. Stored (4.1V for 2 months at RT)

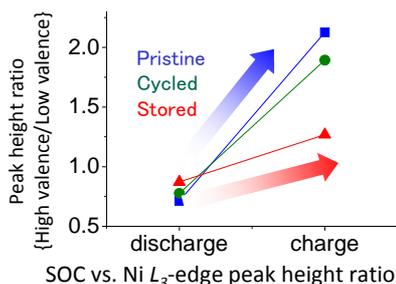
→ Cathodes extracted from samples 1-3 were charged or discharged in half cells and analyzed by XAFS and STEM.

Results of XAFS



Ni L_3 -edge XANES spectra of NCA cathode surface (Total electron yield)

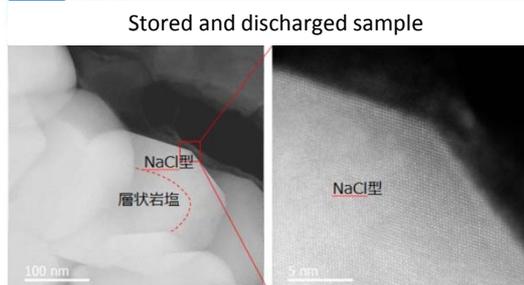
- Ni oxidation by charging process was clearly observed
- Stored sample showed less change in valence population than the other two samples



Slope: Pristine > Cycled >> Stored

Cycle and storage tests increased the amount of resistance phase which doesn't contribute to redox reaction.

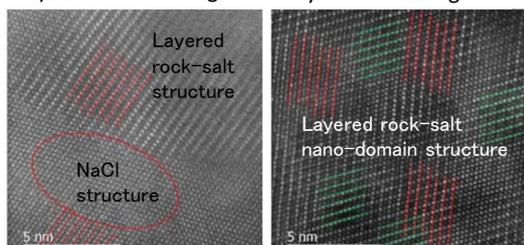
HAADF-STEM images



Inactive NaCl structure was observed at the surface of NCA down to ca. 50nm deep.

Cycled and discharged

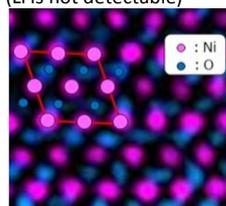
Cycled and charged



Structural difference dependent on SOC was observed.

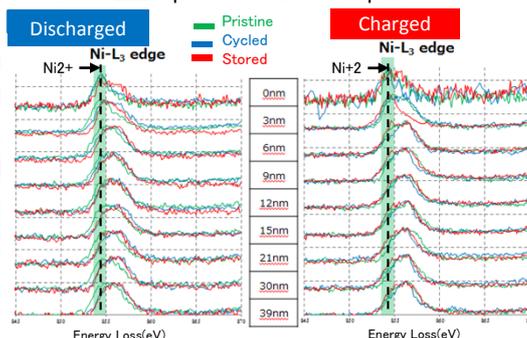
EDS atomic column mapping (NCA[010]) and EELS

EDS mapping of Ni_K + O_K (Li is not detectable)



NaCl structure was observed.

EELS spectra at various depths

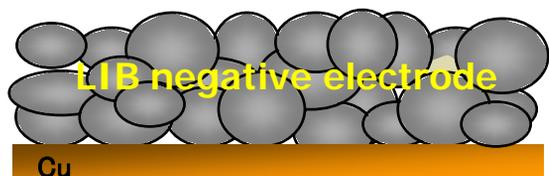


- Consistent result with XAFS.
- Stored and discharged sample had an NaCl structure but showed higher valence state of Ni than bivalence.

- Stored and discharged sample had a thick surface layer of NaCl structure with a thickness of ca. 50nm where Ni was nearly trivalent ($\text{Li}_x\text{Ni}_{1-x}\text{O}$, $X=0.5$).
- Cycle-tested sample had nano-domain structure, whose repeated growth and granulation might result in the gradual increase in the domain of NaCl structure.

Bulk analysis of SEI film on the LIB negative electrode

This article shows bulk analyses of SEI (solid electrolyte interface) on the negative electrodes before (Fresh) and after charge-discharge cycles (After cycles).



Bulk analyses (1)Fresh (2)After cycles

ICP-AES, IC, ^1H NMR, ^7Li NMR

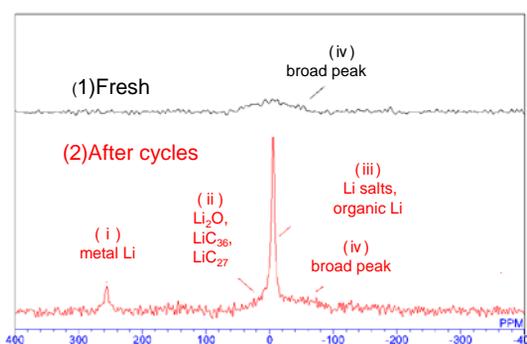
ICP-AES

Quantitative analysis of Li in the negative electrodes

Element	(1)Fresh ($\mu\text{g/g}$)	(2)After cycles ($\mu\text{g/g}$)
Li	7630	12500

^7Li -NMR

Compositional analysis of Lithium compounds in the negative electrodes



Results of ^7Li -NMR (After cycles)

Content	Chemical shift (ppm)	Peak width (ppm)	Atomic ratio (atom %)
(i) Metal Li	256.3	8.2	8
(ii) Li_2O , LiC_{36} , LiC_{27}	3.6	23.8	8
(iii) Li salts, organic Li	- 5.2	5.3	34
(iv) This peak consists of (ii) and (iii)	- 43.9	128.0	51

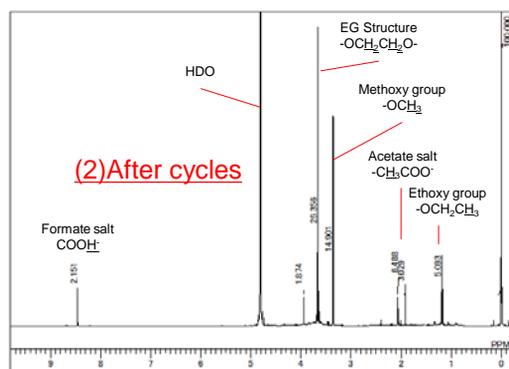
IC

Quantitative analysis of anions in the negative electrode extracts(H_2O)

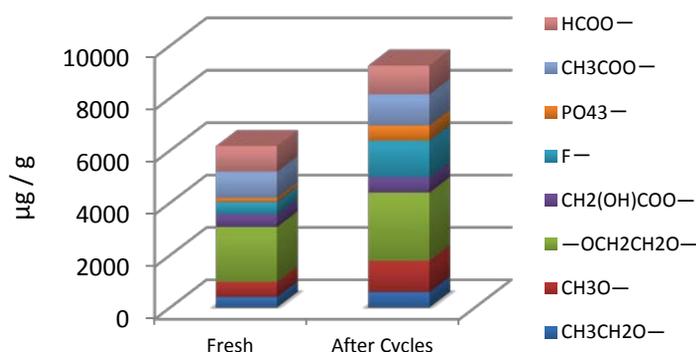
Ions	(1) Fresh ($\mu\text{g/g}$)	(2) After cycles ($\mu\text{g/g}$)
F^-	470	1400
PO_4^{3-}	160	570
CH_3COO^-	1000	1200
HCOO^-	980	1100

^1H -NMR

Quantitative analysis of organic compounds in the negative electrode extracts(D_2O)



Component of SEI estimated from ^1H -NMR and IC

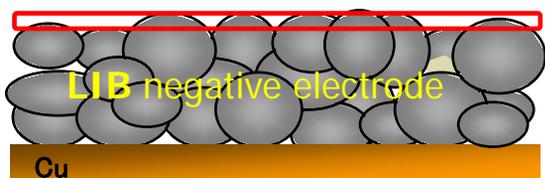


Partial structure	(1) Fresh ($\mu\text{g/g}$)	(2) After cycles ($\mu\text{g/g}$)
$\text{CH}_3\text{CH}_2\text{O}-$	400	580
$\text{CH}_3\text{O}-$	570	1200
$-\text{OCH}_2\text{CH}_2\text{O}-$	2100	2600
$\text{CH}_2(\text{OH})\text{COO}^-$	480	590

From bulk analyses, chemical composition of SEI was determined. Metal Li, F^- , PO_4^{3-} and $\text{CH}_3\text{O}-$ were increased after charge-discharge cycles .

Surface analysis of SEI film on the LIB negative electrode

This article shows surface analyses of SEI (solid electrolyte interface) on the negative electrodes before (Fresh) and after charge-discharge cycles (After cycles).



Surface analyses (1)Fresh (2)After cycles

FT-IR, STEM-EDX, XPS, TOF-SIMS

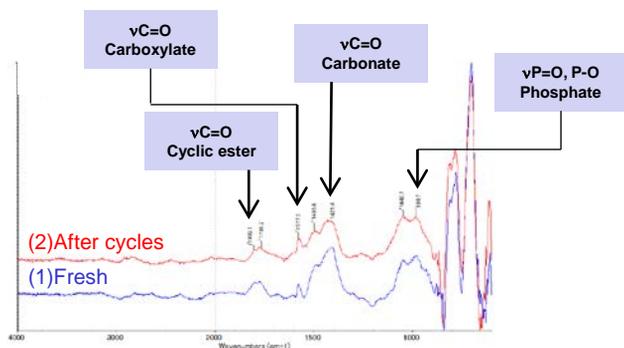
STEM-EDX

Thin layer of SEI was observed by STEM-EDX and EELS

FT-IR

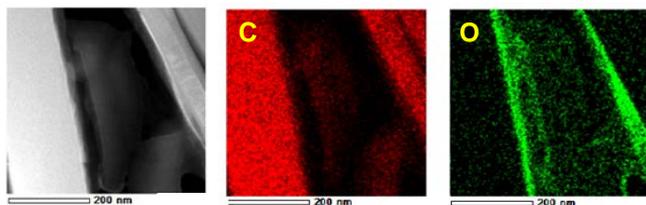
Functional groups and the chemical structure of SEI (~1 μ m depth) were analyzed by FT-IR

There is no difference in the composition between (1)Fresh and (2)After cycles.



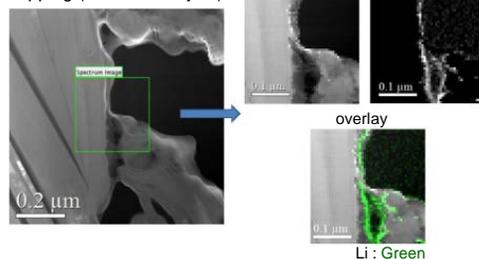
HAADF-STEM Image

EDX mapping (filtered)



EELS mapping (Area of Analysis)

HAADF-STEM Image EELS mapping of Li

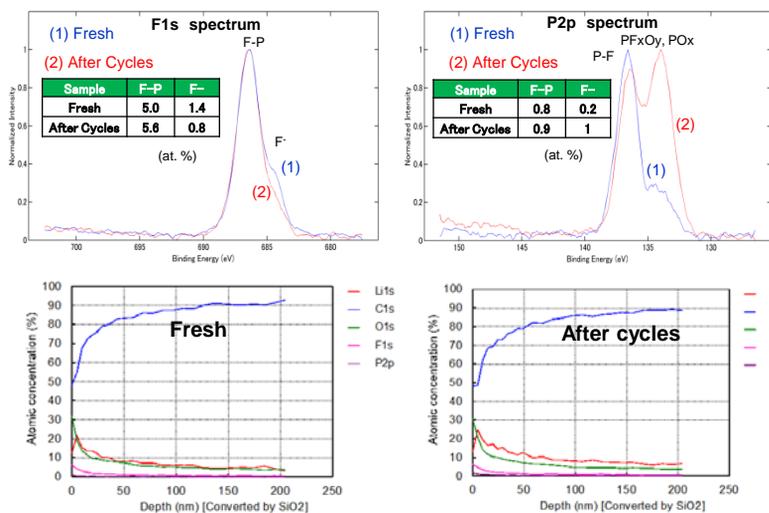


XPS

Elemental composition, chemical state (~10 nm) and SEI thickness (~200 nm) were analyzed by XPS.

TOF-SIMS

Chemical structure of SEI was analyzed by TOF-SIMS.



Fresh negative electrode depth profile

After cycle negative electrode depth profile

Sample	Characteristic components
Fresh	<ul style="list-style-type: none"> ✓ Li₂CO₃ ✓ LiF ✓ Carboxylic acid or ester ⇒ <u>early stage of SEI</u>
After Cycles	<ul style="list-style-type: none"> ✓ PO₂ ✓ PF_xO_y ✓ Ethylene glycol structure ✓ Al ⇒ <u>Decomposition product of the electrolyte, elution from positive electrode collector</u>

From surface analyses, chemical composition of SEI was determined. SEI includes Li, C, O, F and small amount of P.



RBS / NRA / PIXE depth profile of LIB positive electrode

As for the analysis of highly-active materials, such as charged-state lithium ion battery (LIB) electrodes, it is necessary to reduce the change of properties during the measurement. With ion scattering analysis, as typified by RBS, composition depth profile can be obtained without using ion etching, which may cause sample degradation. Here, we show the example of compositional depth profile of LIB positive electrode, applying RBS / NRA / PIXE analysis.

Sample



OSample

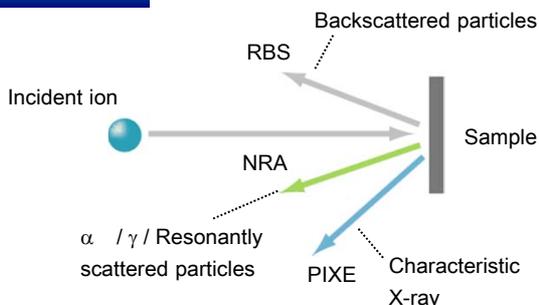
LIB positive electrode : LiNiMnCoO_x

RBS : Rutherford Backscattering Spectrometry
- Accurate composition depth profile

NRA : Nuclear Reaction Analysis
- Li quantification
Li information depth : $\sim 30 \mu\text{m}$
- Enhance O sensitivity

PIXE : Particle Induced X-ray Emission
- Separate adjacent, heavy elements

Principle

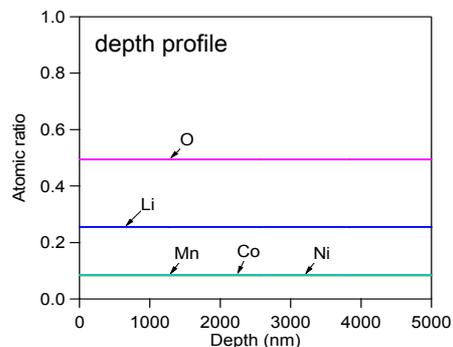
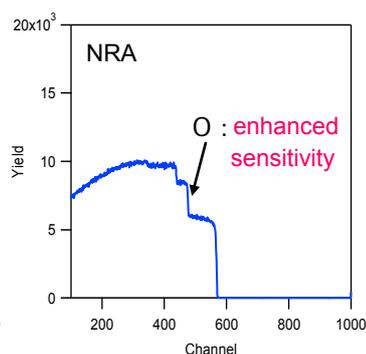
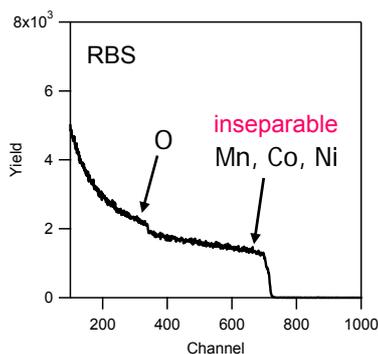


RBS / NRA / PIXE :

Depth profile without using ion etching

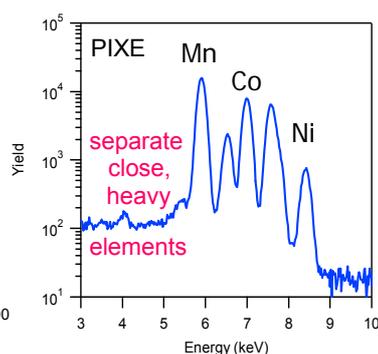
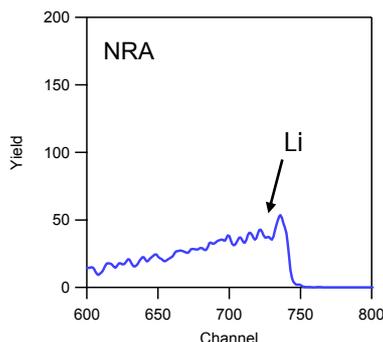
- Reduce sample degradation against highly-active materials

LiNiMnCoO_x Depth Profile



Atomic ratio (normalized by Li content)

Li	Mn	Co	Ni	O
1	0.33	0.33	0.33	1.94

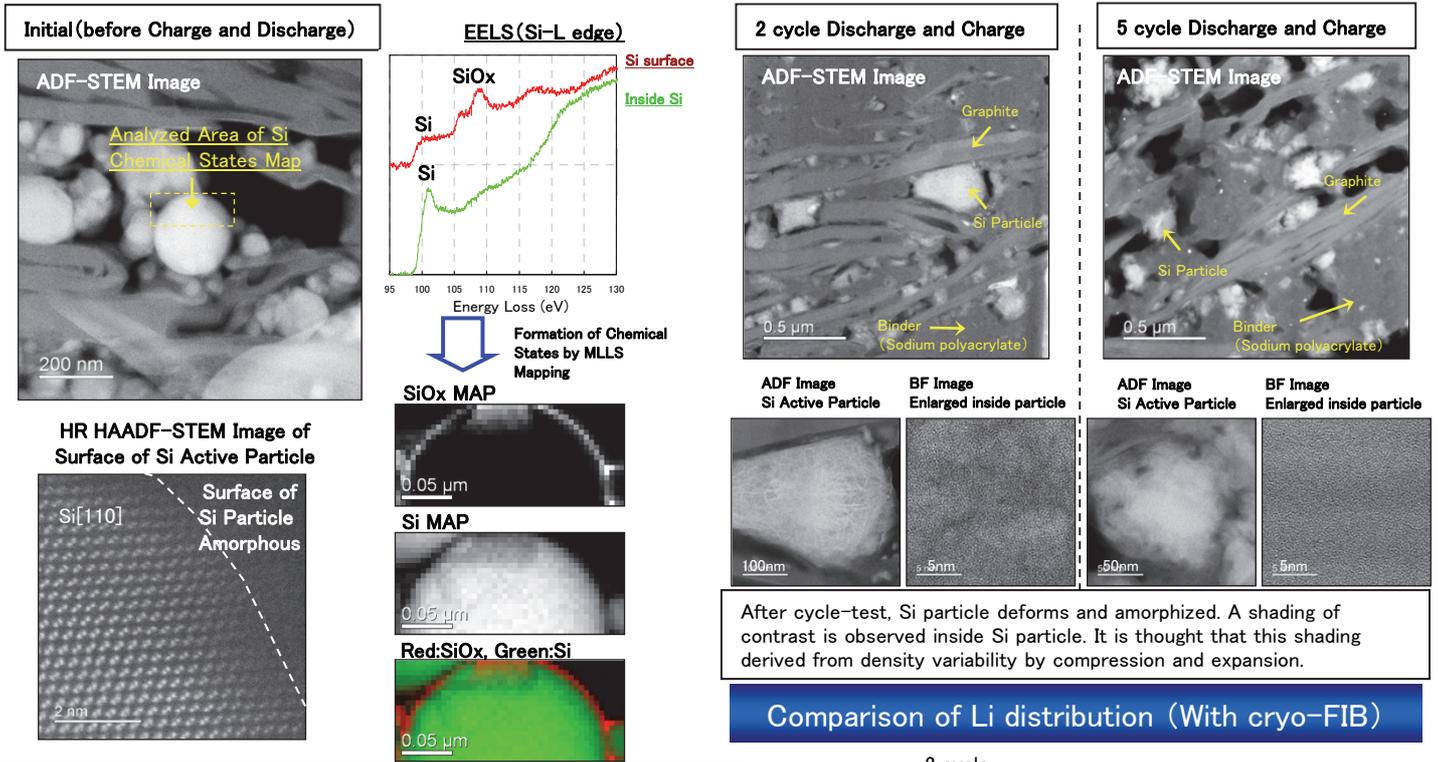


- Accurate composition, including Li, O
- Analysis without air exposure
- Information depth of Li : $\sim 30 \mu\text{m}$

Structure comparison of Si negative electrodes of LIB throughout cycle test by STEM

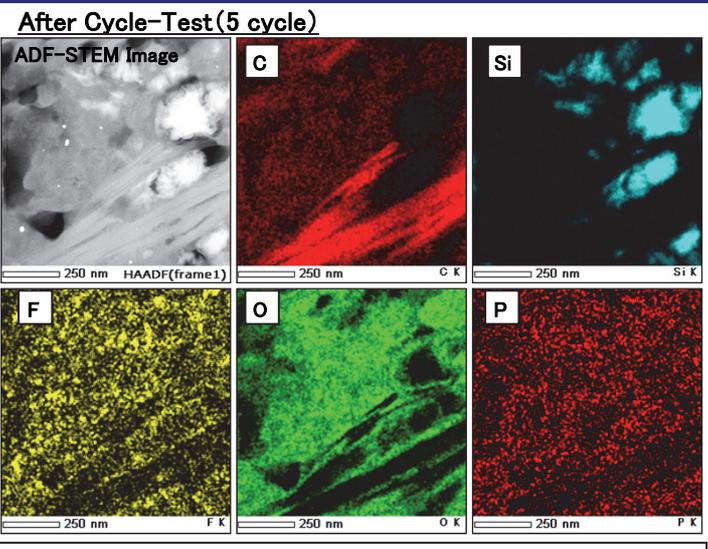
Spherical Aberration corrected STEM enables us to analyze crystal structure, elemental distribution and chemical states at ultra-fine area for Si active particle in negative electrode of LIB, which combine Si nano-particle and Graphite.

Evaluation of Crystal Structure by HR-STEM Observation and Chemical States with EELS



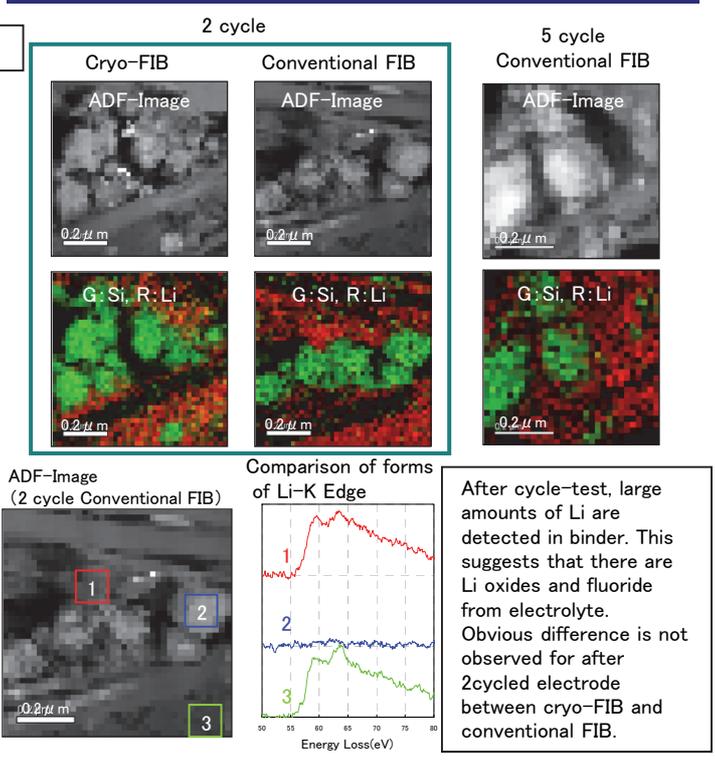
Amorphous native oxide layer is observed at surface of Si particle at initial.

Evaluation of distribution of Electrolyte Components inside Electrode (STEM-EDX)



In the electrode after cycle-test, large amounts of O, F and few P originated from electrolyte at binder are detected.

Comparison of Li distribution (With cryo-FIB)

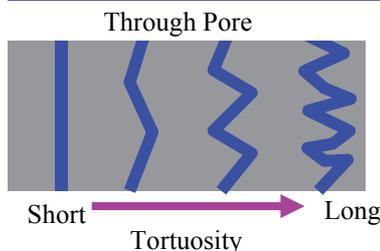


Sample Courtesy : Tokyo Univ. of Sci. Komaba Laboratory

Measurement of tortuosity of porous materials

Tortuosity have implications for the performance of porous materials (e.g. the battery separator film used in the lithium-ion secondary battery, the carbon paper used in the fuel cell), as well as pore size distribution, specific surface area, porosity and permeability. Under the assumption of the laminar flow in cylindrical pore, tortuosity can be estimated by Kozeny-Carman equation.

Definition and calculations



Mercury intrusion porosimetry
N₂ or Kr gas adsorption measurements
Air permeability measurements

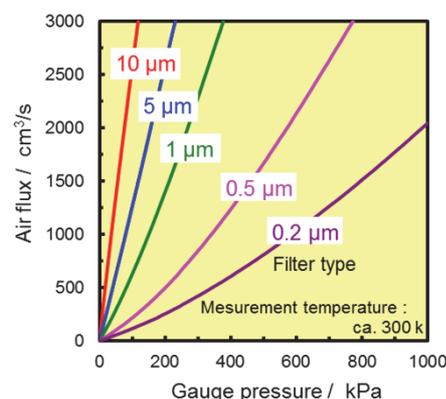
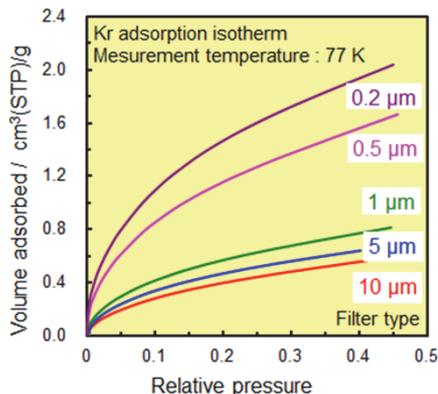
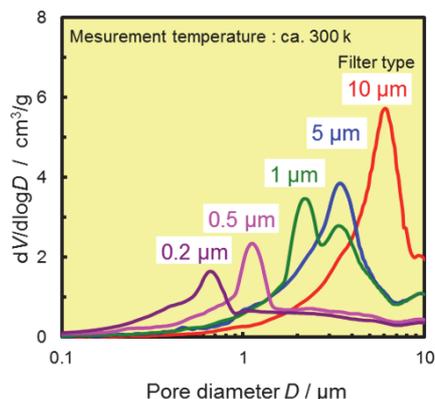
Specific pore volume, Porosity
Specific surface area by BET method
Darcy friction factor

Kozeny-Carman equation

$$\frac{l_e}{l_d} = \sqrt{\frac{\varepsilon}{2k}} \left(\frac{V_p}{S_{BET}} \right)$$

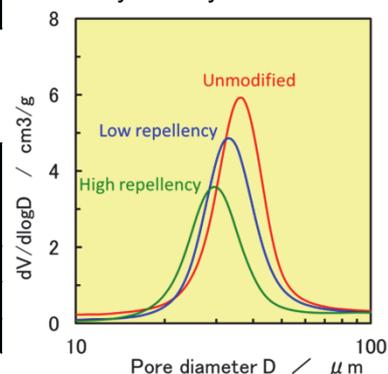
l_e : Pore pathway, l_d : Sample thickness
 V_p : Specific volume of pore, ε : Porosity,
 S_{BET} : Specific surface area by BET method
 k : Darcy friction factor

Separation membranes (Simulation of separators used in the lithium ion battery)



Filter type	Specific pore volume V_p (cm ³ /g)	Specific surface area S_{BET} (m ² /g)	Porosity ε	Air permeability k (Darcy)	Tortuosity
10 μm	2.1	2.2	0.46	0.071	1.7
5 μm	2.0	2.5	0.60	0.028	2.6
1 μm	1.9	2.9	0.53	0.012	3.1
0.5 μm	1.2	5.9	0.60	0.003	2.0
0.2 μm	1.2	7.5	0.64	0.001	2.9

For separation membranes, parameters except tortuosity are related to the pore size. On the other hand, tortuosity is not related to the other parameters. Therefore, it is necessary to obtain the pore volume, porosity and permeability independently, in order to estimate tortuosity exactly.



Carbon papers used in the fuel cell

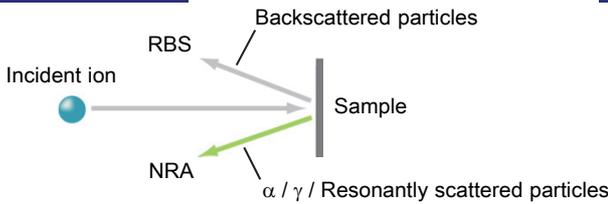
Sample	Specific pore volume V_p (cm ³ /g)	Specific surface area S_{BET} (m ² /g)	Porosity ε	Air permeability k (Darcy)	Tortuosity
Unmodified	1.7	0.30	0.64	3.3	1.8
Low repellency	1.4	0.16	0.56	3.1	2.6
High repellency	1.1	0.21	0.42	1.5	2.0

For water-repellent carbon papers, porosity and air permeability become small, as the pore is filled by the water-repellent resin (polytetrafluoroethylene, PTFE). For low water-repellent carbon paper, tortuosity becomes the maximum value, which shows the construction of the most complicated pore structure.

RBS/NRA depth profile of LIB negative electrode after charge – discharge cycles

Lithium Ion Battery (LIB) negative electrode can be analyzed by RBS / NRA method. Keeping charge - discharge state, depth profile can be obtained from surface to bulk. Generally, the quantitative value is considered to be as accurate as ICP-AES.

Principle



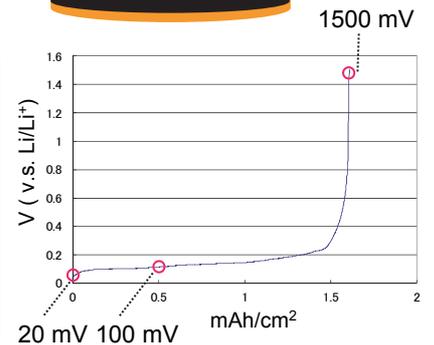
- RBS : Rutherford Backscattering Spectrometry
 - Accurate composition depth profile
- NRA : Nuclear Reaction Analysis
 - Li quantification (information depth : ~ 30 μm)

RBS, NRA : do not need ion etching for depth profile
 → **Accurate depth information without sample degradation**

Charge - discharge characteristic

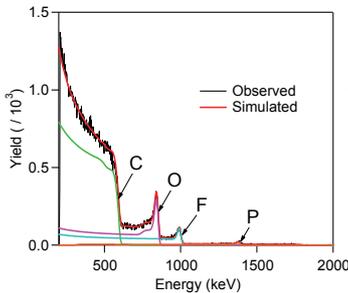
OSample
 LIB negative electrode : Graphite

Charging potential (v.s. Li / Li ⁺)	State
20 mV	Fully Charged
100 mV	Intermediate
1500 mV	Fully Discharged

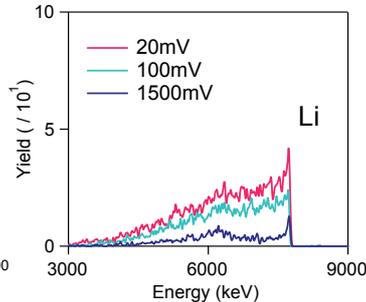


Adjusted charging potential, each sample is introduced into RBS / NRA instrument, **without air exposure**.

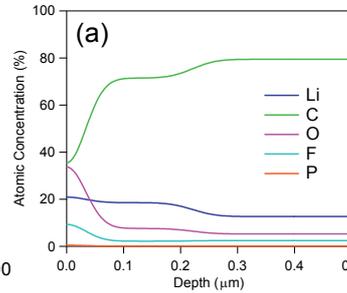
Composition of electrode at each charging potential



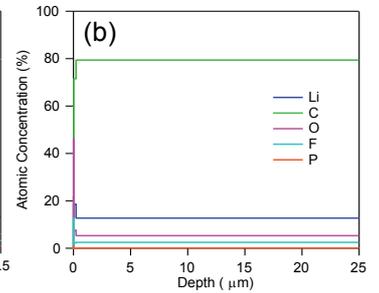
RBS spectrum (20 mV)



NRA spectra



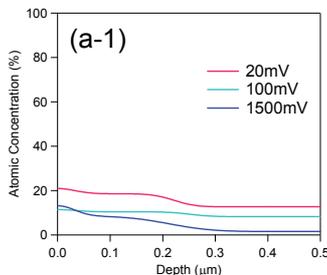
Depth profile (20 mV) (a) : surface, (b) : bulk



(a) Li, O, F, P concentration is high at surface region

(b) Li concentration in deeper region is constant

(a) Surface



Comparison of (a-1) : Li, (a-2) : O depth profile

- **Li concentration : gradually decrease till ~ 250 nm**
- **O concentration at surface : 20 mV, 100 mV > 1500 mV**

(b) Bulk composition

Charging potential [mV]	atomic%					C / Li	Estimated structure
	Li	C	O	F	P		
20	12.7	79.4	5.3	2.5	0.1	6.3	LiC ₆
100	8.3	84.2	5.4	2.0	0.1	10.1	LiC ₁₂
1500	1.6	93.5	2.1	2.7	0.1	58.8	C

bulk composition (atomic%), and C/Li ratio

• **High accurate composition**※ → comparable with structure directly

※ General accuracy of RBS/NRA analysis : ~±3%

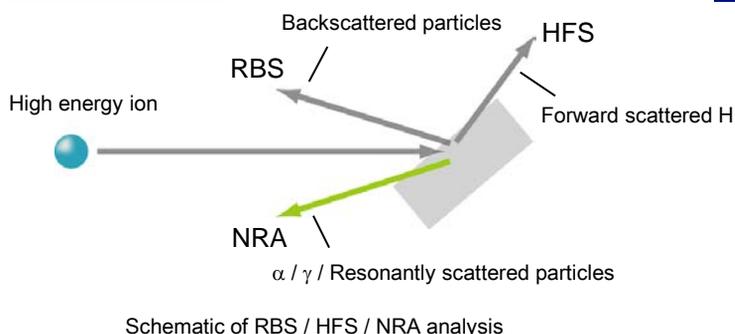
RBS / NRA - Accurate depth profile can be obtained, from surface to bulk region

RBS / HFS / NRA analysis for oxide-based solid electrolyte

Using ion scattering, as typified by RBS, composition depth profile can be obtained for thin films with various thickness, from ultrathin to thick. Note that accurate composition, including hydrogen can be obtained. In addition, light elements like Li, can also be quantified using nuclear reaction.

Here, solid electrolyte compositional analysis is presented, which is considered to be the key material for all-solid-state rechargeable lithium batteries.

Principle



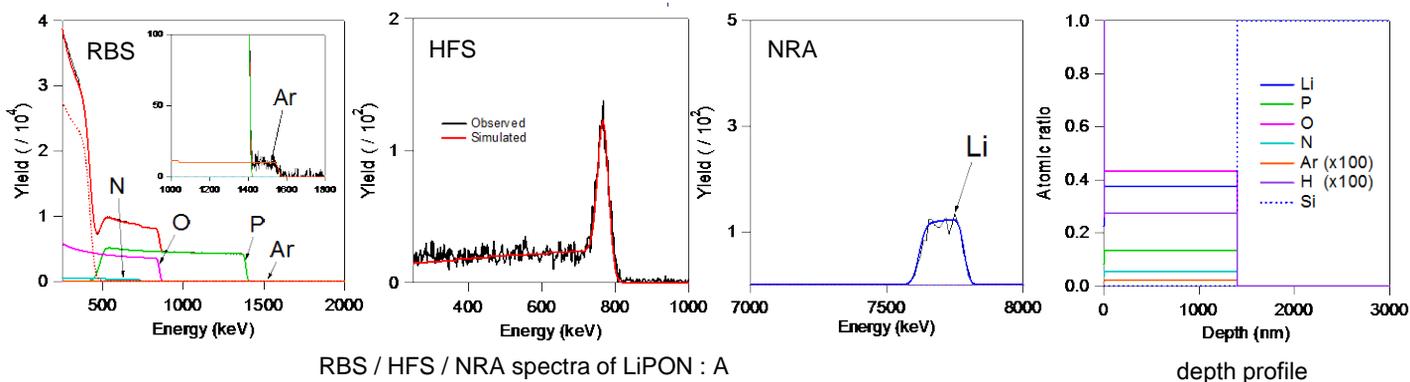
RBS : Rutherford Backscattering Spectrometry
 HFS : Hydrogen Forward scattering Spectrometry
 NRA : Nuclear Reaction Analysis

Sample



sample	A	B
deposition	Sputtering	
gas	N ₂	
target	Li ₃ PO ₄	
gas pressure	high	low
thickness	1.36μm	1.52μm
heating	-	

LiPON depth profile



- P / O / N ratio : RBS. Ar is also detected.
- H and Li are quantified by HFS and NRA, respectively. LiPON composition was determined using those 3 spectra.

Sample	atomic%					
	Li	P	O	N	Ar	H
A	37.5	13.4	43.3	5.5	0.02	0.3
B	38.1	13.5	44.2	3.9	0.03	0.2

• N content is different between the samples.

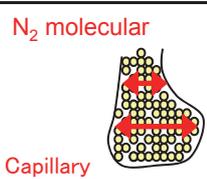
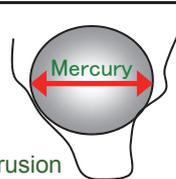
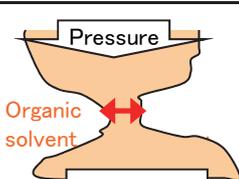
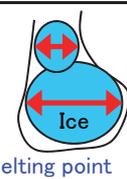
- Accurate composition, including Li and H
- Can be measured under an inert gas atmosphere
- Information depth of Li : ~ 30nm

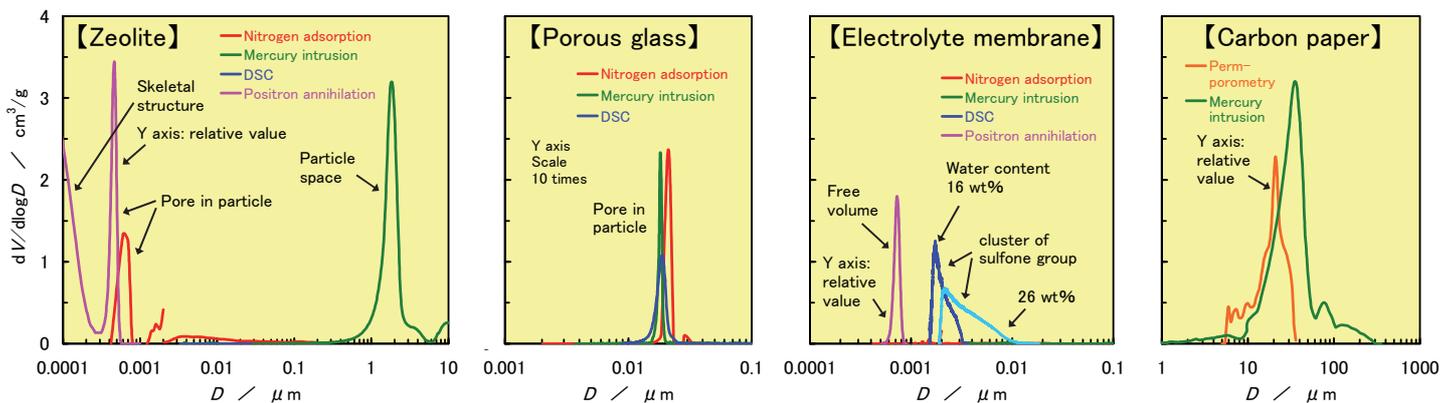
To investigate the physical properties of the surface ~Measurement techniques of surface property~

In the measurement of the pore size distribution, specific surface area and water vapor adsorption characteristics, it is important to select the appropriate measurement techniques in accordance with surface chemical state and pore size.

Pore size distribution

Comparison method: TEM, SEM, AFM, X-ray etc.

Method	Nitrogen adsorption	Mercury intrusion	Perm-porometry	DSC	Positron annihilation
Pore diameter	0.4 ~ 200 nm	4 nm~400 μm	0.2~200 μm	2~200 nm	0.2~5 nm
Pore shape	Open	Open	Through	Open	Closed
Limitation	Dry	Dry	Film	Wet	Dry / Film
Pore image Probe image					
Pore diameter	Capillary condensation	Intrusion	Pressure Organic solvent	Melting point depression	Life time
Quantitatively	○	○	×	○	×
Main target	Activate Carbon Zeolite / Silica-gel	Electrode Separator	Carbon paper Separation film	Electrolyte Wet material	Polymer / Silica Low-k / Metal



Micro-pores in zeolite or activated carbon → Nitrogen gas adsorption
Inter-particle pore → Mercury intrusion
Skeletal structure → PALS

Pore size of the inorganic material substantially coincident with each method

Water cluster size → DSC
Free Volume → PALS

Neck diameter to dominate the fluid permeability → Perm-porometry

Surface area

Method	N ₂ adsorption	Kr adsorption	CO pulse
Obtained result	BET method surface area 2~3 m ² /g <	BET method < 2~3 m ² /g 100 times sensitive	Effective surface area
Adsorption type	Physical	Physical	Chemical
Main Target	Activate carbon Zeolite Silica-gel	Graphite Small sample Thin film	Supported metal (Pt, Pd etc.)

Water vapor adsorption

Method	Volumetric	Gravimetric
Detector	Pressure	Mass
Condition	Water vapor only	Water vapor + Air
Temperature	5~100 °C	25~80 °C
Humidity	Relative pressure 0~1	20~80%RH (Temperature dependence)
Strong point	Rapid equilibration	Under real environment

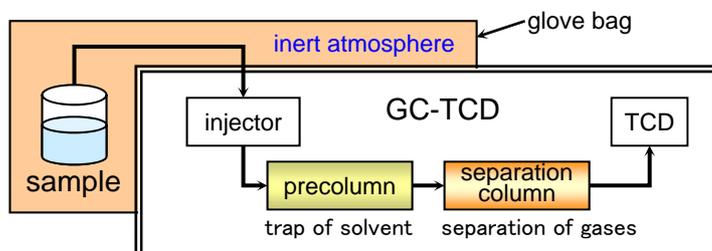
Quantitative Analysis of Dissolved Gases in Liquid

X-14

Quantitative analysis of dissolved gases in liquid is a key process for quality control in manufacturing liquid products. Quick and appropriate separation of the liquid and the dissolved gases is necessary to obtain the accurate contents of the gases. The time dependence of the dissolved gas concentration and the temperature dependence of the solubility of gases can be determined by the specified GC.

Analytical procedure

1. Injection of the sample solution to GC.
2. Trap of solvent in the precolumn to make the only dissolved gas go to the separation column.
3. Separation of H₂, O₂, N₂, and etc. by separation column.
4. Detection by Thermal Conductivity Detector.

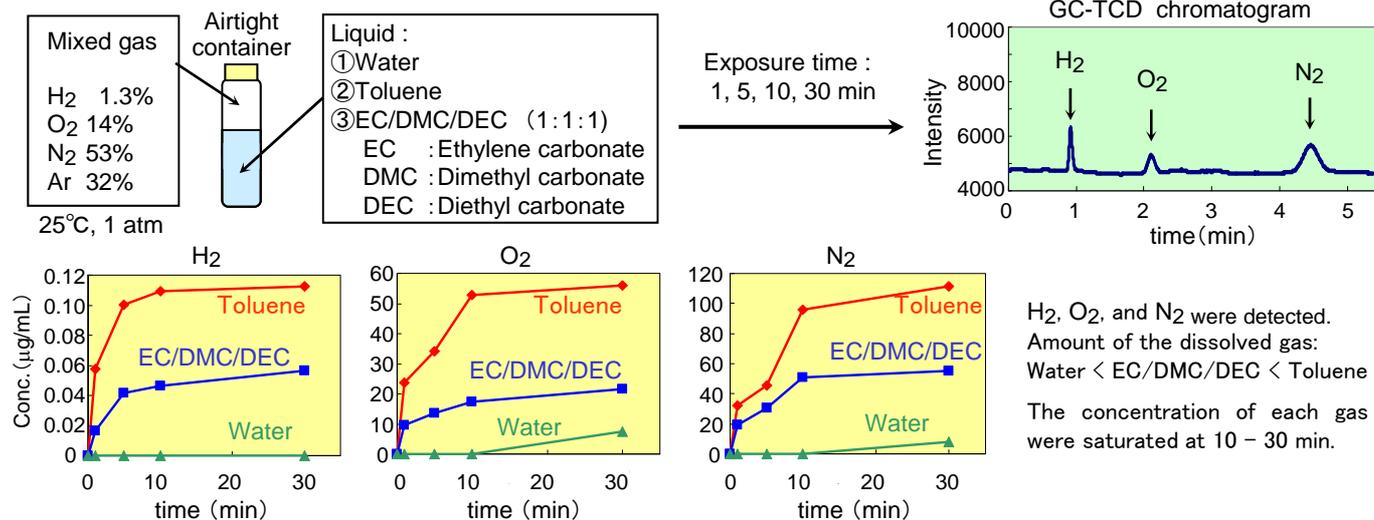


Objective gas : H₂, O₂, N₂, CO₂, CO, Hydrocarbon(C₁₋₂)
Sensitivity : N₂, O₂ ⇒ 1~10 µg/mL

O₂ and N₂ should be sampled and injected to GC under inert atmosphere preventing air contamination

Analysis of dissolved H₂, O₂, and N₂ in liquid material

Pure water, Toluene, and EC/DMC/DEC were exposed to the mixed gas of H₂, O₂, N₂ and Ar. The dissolved gases were analyzed after 1, 5, 10, and 30 min.

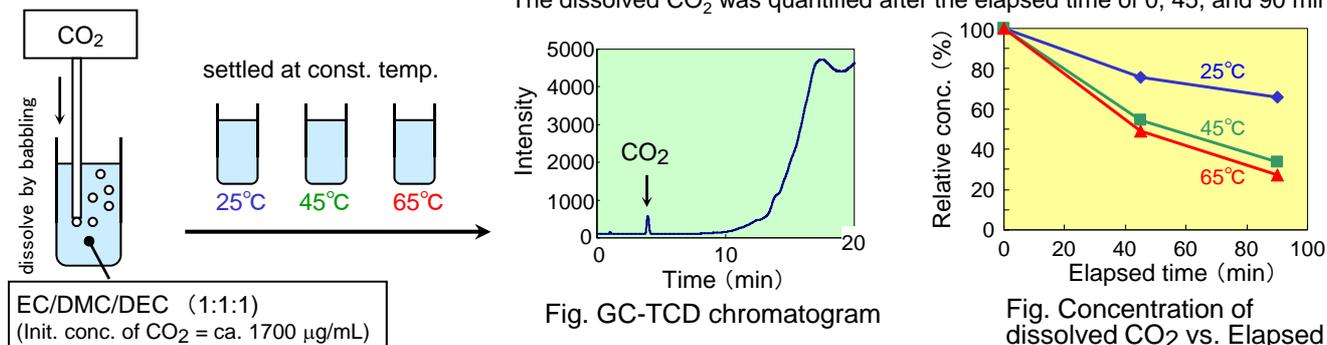


H₂, O₂, and N₂ were detected.
Amount of the dissolved gas:
Water < EC/DMC/DEC < Toluene
The concentration of each gas were saturated at 10 - 30 min.

Fig. Time dependence of the dissolved gas in liquids

Temperature dependence of CO₂ gas solubility

CO₂ was dissolved in EC/DMC/DEC by bubbling, then settled at 25, 45, or 65 °C. The dissolved CO₂ was quantified after the elapsed time of 0, 45, and 90 min.



The amount of the dissolved CO₂ in EC/DMC/DEC was reduced with the elapsed time.
The reduction rate increased with the temperature increase.

Generated gas Analysis of Lithium Ion Battery

Generated gas Analysis of Lithium Ion Battery

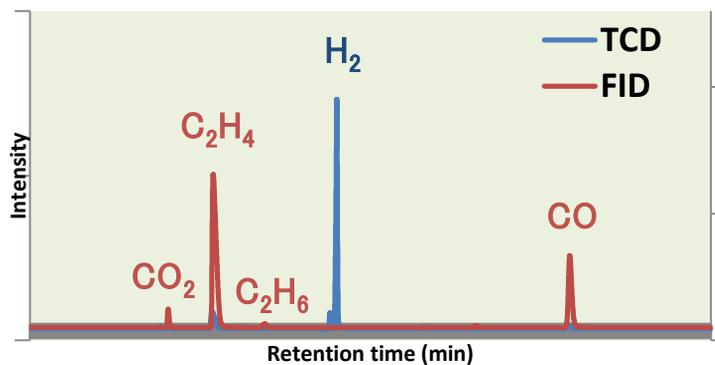
There are concerns with generating various gases from LIB containing organic solvents. Toray Research Center, Inc. is able to manufacture LIB by way of trial and totally analyze and evaluate including gas analysis.

Trial production LIB



laminated winding type

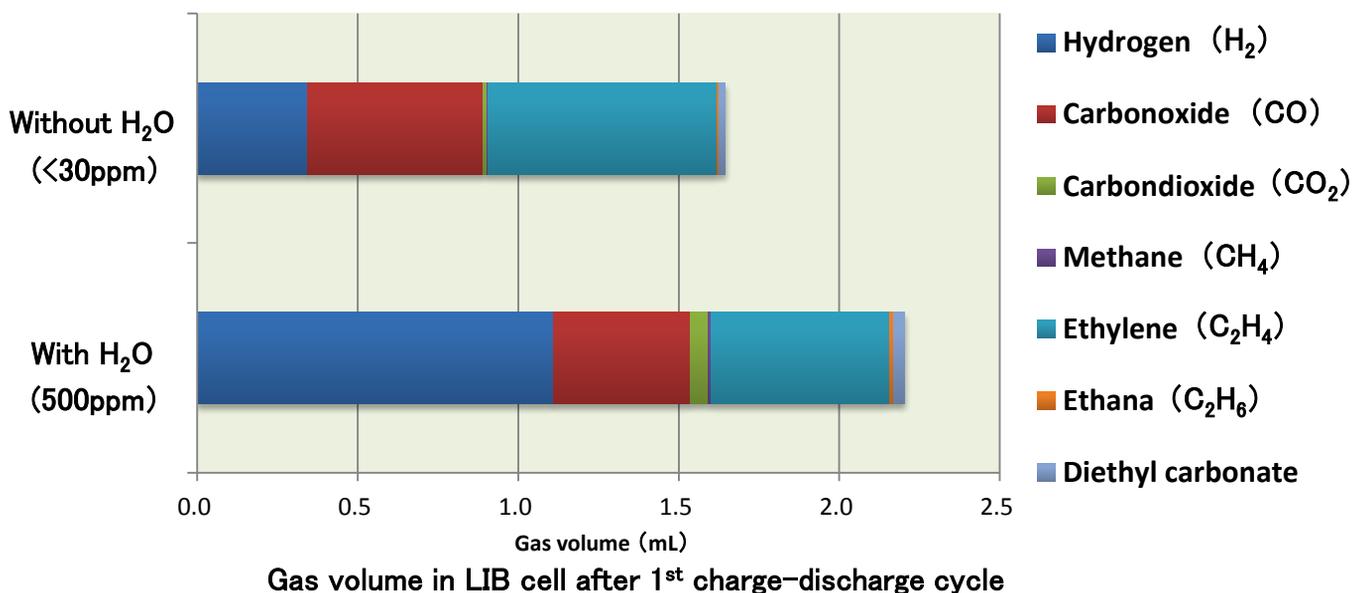
Gas sampling under inert atmosphere



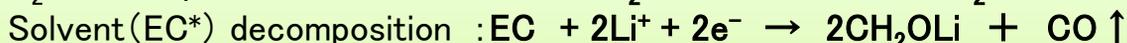
Gas chromatograph of generated gas in LIB

Effect of H₂O for gas generation in 1st charge-discharge cycle of LIB

Generated gases from the trial LIB after the first charge and discharge cycle were analyzed by GC and GC/MS. Two LIBs which are composed of the dehydrated and the not dehydrated components were prepared.



Gas generation mechanism



*EC: Ethylene carbonate