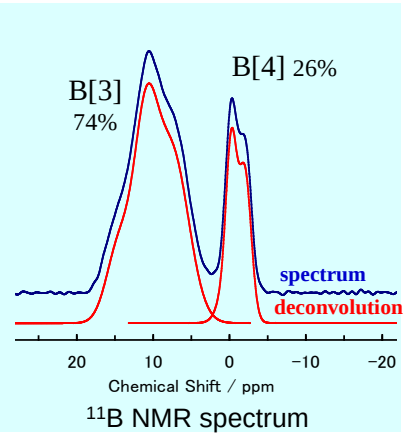
Analyzing inorganic materials.

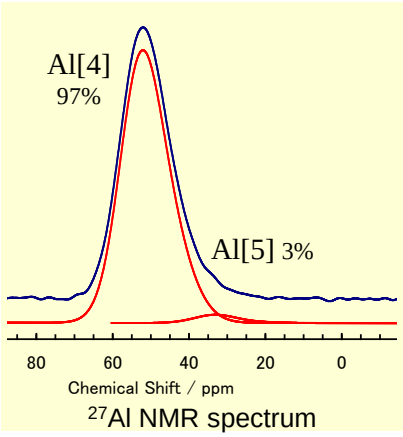
Many of inorganic materials like glasses and zeolites consist of elements, such as Si, Al, and B. With the solid-state NMR, it is able to acquire the information of neighboring structure combined to Si and information of the coordination number about Al and B.

Chemical structure of alumino-borosilicate glass

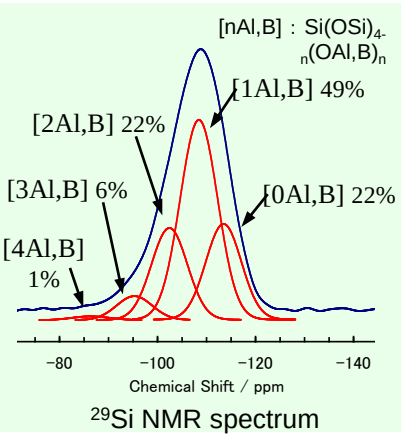
In order to perform structural analyses of the alumino-borosilicate glass, ^{11}B, ^{27}Al, and ^{29}Si NMR measurements were carried out. It was possible to estimate the composition ratios of the components for the different coordination number around Al and B, and for the various neighbor structure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



^{11}B NMR spectrum



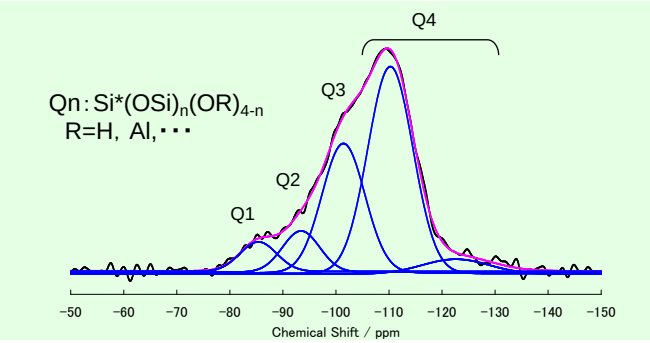
^{27}Al NMR spectrum



^{29}Si NMR spectrum

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	SiO_2/Al_2O_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.

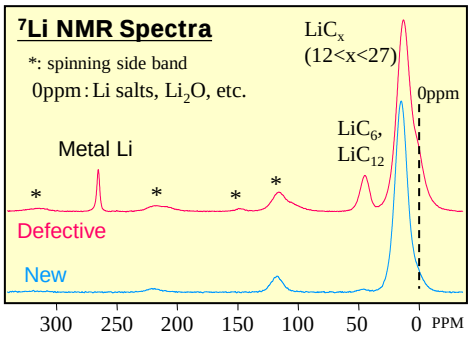
The chemical state information in the anode and cathode of lithium ion battery (LIB) can be obtained quantitatively by solid-state NMR. The sampling in the inert atmosphere enables the analysis without the damage caused by the atmospheric air and moisture exposure of samples.

Chemical state of lithium in anodes

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

From ^{7}Li 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	LiC_6, 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 ^{6}Li.

The advantage of ^{6}Li is the smaller effect of quadrupole interaction than ^{7}Li.

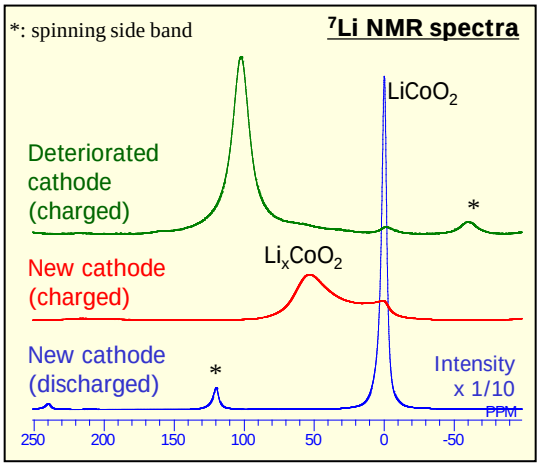
Although natural abundance ratio of ^{6}Li is as low as 7.6% and then the sensitivity is very low, it is possible to take full advantage of ^{6}Li with usage of ^{6}Li enrich samples

Chemical state of lithium in cathodes

For the cathode of LIB (mixture of $LiCoO_2$ and $Li(Co,Ni,Mn)O_2$), in order to assess the difference in chemical states of Li between three conditions, ^{7}Li 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«1) and the charge-discharge efficiency was fallen.

However, the signal of $Li(Co,Ni,Mn)O_2$ 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.



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