Using CO_2 gas for Next–generation Positive–Active slurry

Next-generation Positive-Active Materials
High-Nickel NCM and NCA materials are expected.

Problems with high-nickel positive-electrode active materials

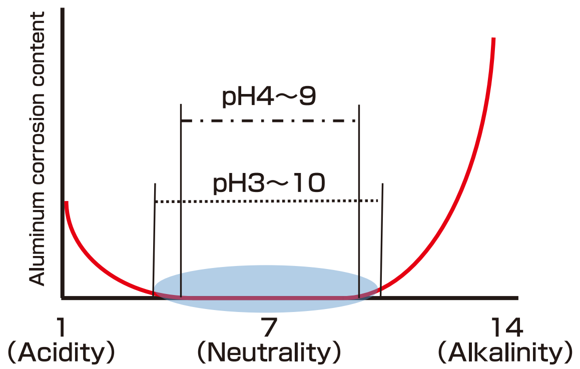
Water-based

Corrosion of the aluminum current collector due to the strongly alkaline slurry

Solvent

PVdF binder slurry turns to gelation

When outside a scope of between pH 3 and 10, the aluminum foil erodes; generating hydrogen gas.



Gelled PVdF slurry

NCA : CB : PVdF=90 : 5 : 5wt.%、
Planetary centrifugal mixer, 2000 rpm, after 30 minutes,
Solvent : NMP

Proposing New Technology

We have troubleshooted and simplified a process for creating next-generation positive-electrode material; utilizing **carbon dioxide gas** and **the cavitation effect**.

- **A range of high-nickel cathode-active materials** selectable.
- Many kind of binders can be selected to design **High-Value Batteries** with high-temperature properties and high output characteristics, etc.

Water-based slurry
Neutralization by carbon dioxide gas and the cavitation effect

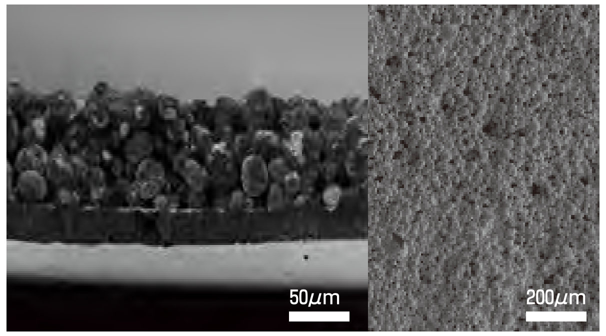
Neutralization reaction by carbon dioxide gas

$$2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$$

Easily neutralized
using the cavitation effect on JET PASTER

Model：JPSS-X

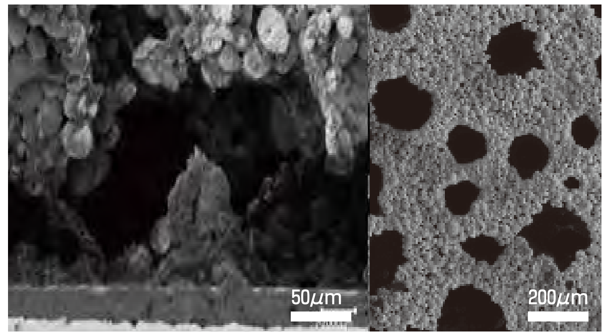
With carbon dioxide gas at pH7.9



Cross section　　Surface

NCA:CB: **Acrylic binder** =92:4:4 (wt.%)

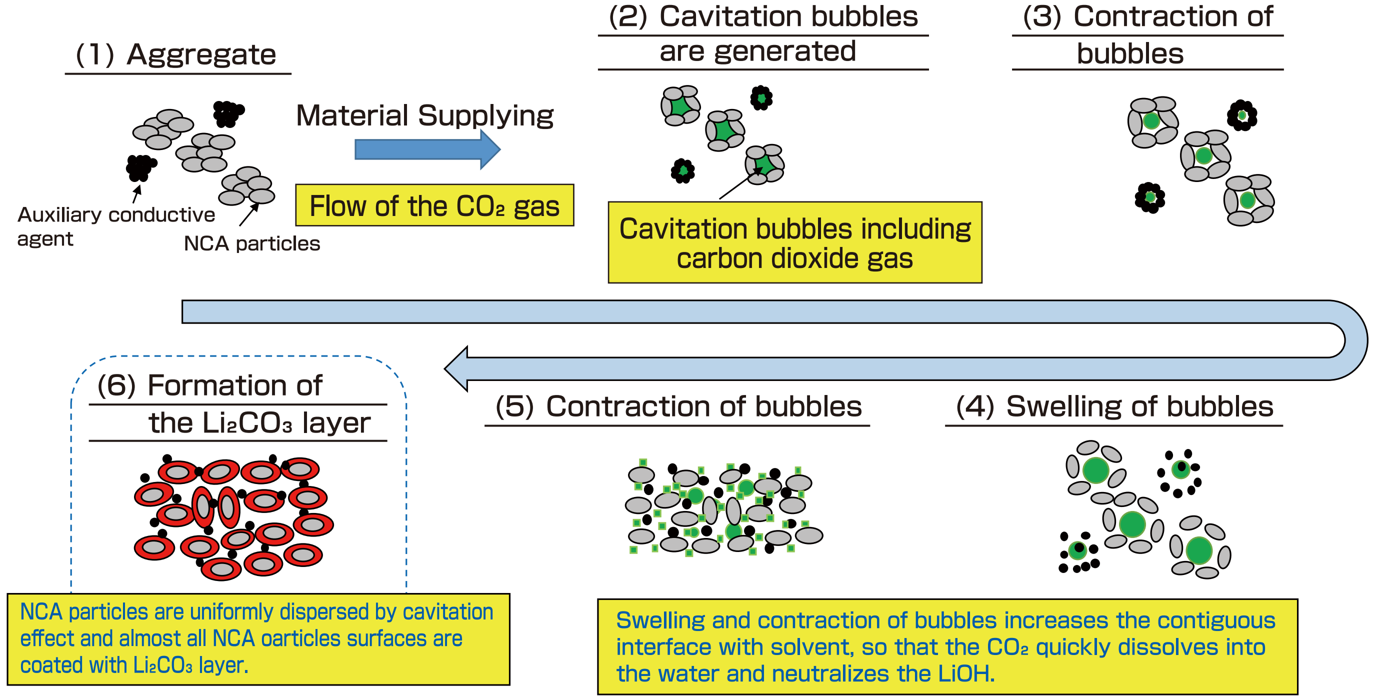
Without carbon dioxide gas pH12.3



Cross section　　Surface

Hydrogen is generated due to the following reaction, which **becomes porous**:
$2Al + 2LiOH + 6H_2O \rightarrow 2Li[AL(OH)_4)] + 3H_2\uparrow$

[The Mechanism of the Carbon Dioxide gas teratment using the Cavitation Effect]



Water-based slurry
A Comparison of Battery Properties and Particle Surface with or without Carbon Dioxide Gas Treatment

Obtained a discharge capacity equivalent to PVDF binder with water-based slurry also.

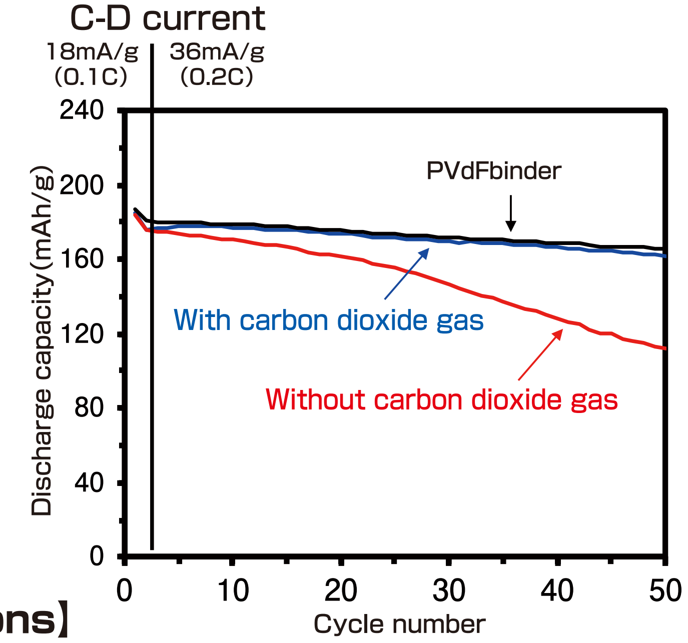
[Conditions]

Composition of positive-electrode slurry
NCA : CB : VGCF : Binder
= 92 : 3.5 : 0.5 : 4 (wt.%)

①Dispersed with carbon dioxide gas treatment using the cavitation effect

②Dispersed without carbon dioxide gas

Applied to coat on Al foil and dry



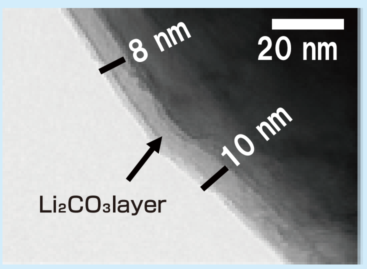
[Battery fabricating conditions]

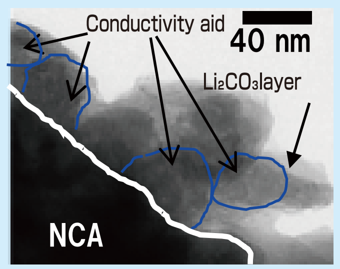
NCA:CB:VGCF:Binder =92:3.5:0.5:4 (wt.%)
Capasity density : 1.4 mAh/cm²
Opposite electrode : Lithium foil
Electrolyte : 1M $LiPF_6$ EC:DEC=1:1 (v/v)
Battery condition : 2032coin cells
Cut-off voltage : 4.2V-2.7V

	Discharged capacity (mAh/g)		
	1st	2nd	50th
With carbon dioxide gas	185	176	162
Without carbon dioxide gas	184	176	112
PVdFbinder	187	181	166

NCA particle surface (TEM image)

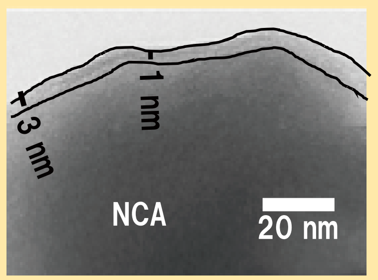
①With carbon dioxide gas





- LiOH reacts with carbon dioxide gas to generate Li_2CO_3 layer
- A conductivity additive is included.

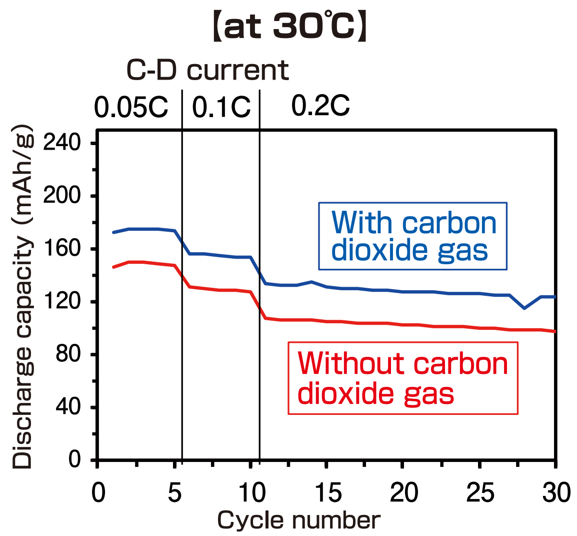
②Without carbon dioxide gas

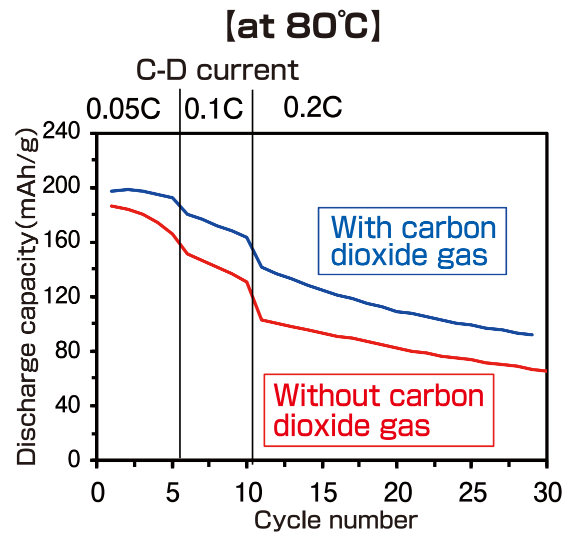


A very thin layer of Li_2CO_3 on the surface of NCA is coated by reacted LiOH with CO_2 in air.

Evaluation with a 1Ah class cell (winding-type laminate cell) (at 30 and 80℃)

High-temperature properties with carbon dioxide gas treatment is much better.



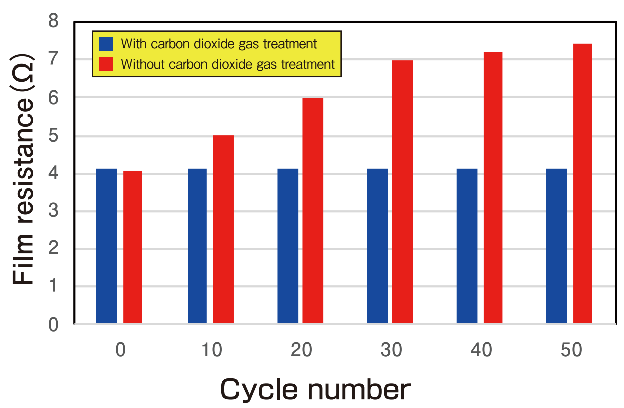


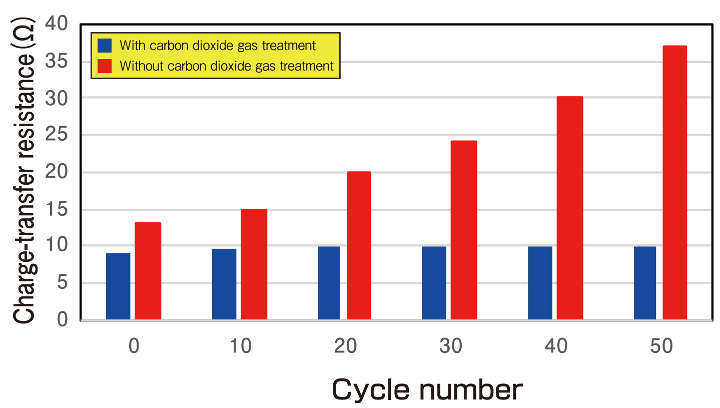
NCA:CB:VGCF:Binder=92:3.5:0.5:4 Opposite electrode: Li pre-doped SiO electrode n/p ratio = 2/1
Electrolyte : 1M $LiPF_6$ EC:DEC = 1:1 (v/v) Capacity of positive electrode :1Ah
Battery : laminated cells

Impedance Comparison

◎Effct of Carbon Dioxide gas treatment

- Neither increase of film resistance nor charge-trasnfer resistance were found.
  →The Li_2CO_3 layer inhibits electrolyte decomposition as well as the reaction between the electrolyte and the surface of active materials.
- Film resistance and charge-transfer resistance are small through cycles.





Water-based Carbon Dioxide gas treatment using JET PASTER

① **Using JET PASTER allows you to fabricate batteries with high-nickel active materials.**

② **Discharge capacity in the charge and discharge test (coin cell: 0.2 C) shown to be equivalent to the electrode fabricated with PVDF/NMP.**

③ **The discharge capacity was also improved compared to the electrode without carbon dioxide gas treatment with a 1Ah winding-type laminate cell.**

④ **It is presumed that both electrolyte decomposition and any increase in impedance are inhibited, since lithium carbonate coats the surface of high-nickel active materials.**

⑤ **It is applicable to active materials such as NCM (523, 622 and 811) and NCA.**

Application to organic slurry

Organic slurry
Application to High-Nickel active materials

[The mechanisms of the positive-electrode slurry turning into gelation]

LiOH dissolves in the small amount of moisture existing in the positive-electrode solvent and active materials and attacks binds, which **creates a double bond.**

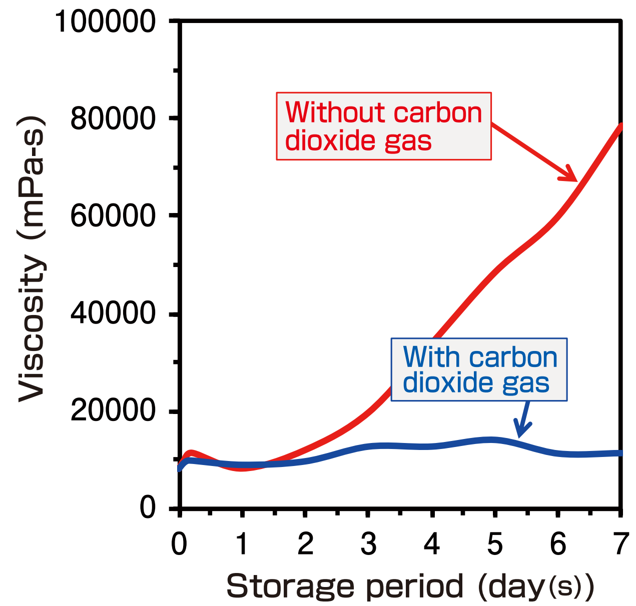
Gelation : $[-(CH_2-CF_2)-]$ + LiOH → $[-(CH=CF)-]$ + LiF + H_2O

Neutralization : $2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$

[Effect of Carbon Dioxide gas]

Carbon dioxide gas can inhibit for LiOH to attack to PVdF and prevent from gelation of PVdF.

- No uniform electrode coating was available when a traditional method was used, since the slurry turns into gelation, whereupon the degree of viscosity rises.
- There is scope to **inhibit slurry turning to gelation** by applying carbon dioxide gas treatment, which extends the **feasible storage duration of slurry considerably**.



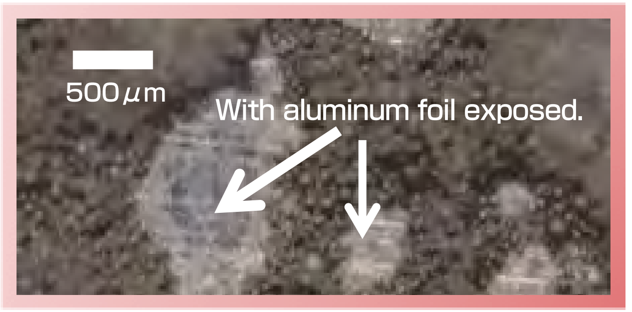
Change in viscosity of NCA slurry using PVdF
(Solid content ratio: 75 wt.%)

[Electrode fabricating conditions]

NCA:CB: PVdF binder =94:2:4 (wt.%)
Capasity density: 2.0 mAh/cm2

An optical microscopic image of the electrode surface with slurry coated to aluminum foil **after seven days** of slurry production

Without carbon dioxide gas treatment



With carbon dioxide gas treatment