Improvement of Hydration Rate of LiOH by LiOH/Mesoporous Carbon Composite for Low-temperature Heat Storage

Introduction

For achieving high energy utilization efficiency

Promotion of utilization of low-temperature heat below 100 °C is required.

Chemical Heat Storage system
(Heat energy is stored and released by reaction heat.)

- ○ High heat storage density
- ○ Long-term heat storage in the form of chemical substances
- ○ No heat loss & No need of thermal insulation
- △ Complex system

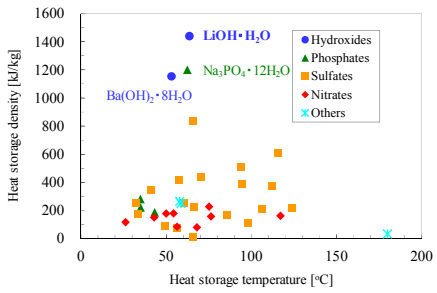


Fig. Relationship between heat storage temperature & heat storage density

	Endothermic temp. [°C]	Endothermic heat [kJ/kg]
$LiOH \cdot H_2O$	**64.13**	**1,440**
$Ba(OH)_2 \cdot 8H_2O$	53.17	1,153
$Na_3PO_4 \cdot 12H_2O$	62.50	1,200

- Large endothermic heat
- Safety
- Simple reaction

$LiOH \cdot H_2O(s) = LiOH(s) + H_2O(g)$
is promising for low-temperature heat storage

Technical problem of $LiOH/LiOH \cdot H_2O$ system :

▲ **Hydration of LiOH proceeded very slowly (Hydration ratio: Only 0.24 in 60 min at 30 °C & 80 %RH).**

= Heat output in heat releasing step is quite low.

Enhancement of hydration rate is essentially required.

In this study:

A combination of LiOH and mesoporous carbon (MPC) was experimentally investigated.

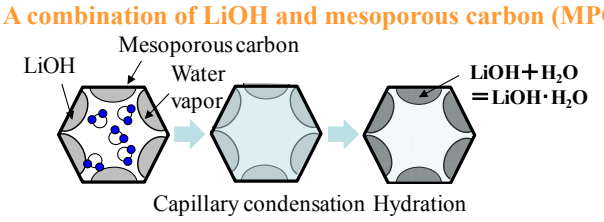


Fig. Concept of this study

We expected
LiOH reacts with water adsorbed in mesopore rapidly.

Experimental

～ Starting material ～

- $LiOH \cdot H_2O$ (Purity: 98 %, Wako Pure Chemical Ind.)
- MPC (CNovel, Toyo Tanso Co., Ltd.)

Table Pore structures of MPC

Mean pore diameter [nm]	BET Surface area [m^2/g]	Total pore volume [cm^3/g]
3.75	1,448	1.36

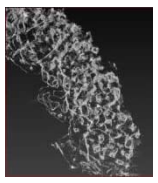
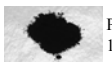


Fig. TEM image of MPC

Features of MPC
- Open pores
- Rapid gas diffusion in pores
- High hydrophilicity



Particle diameter: 1~10 μm

Fig. Appearance of MPC

～ Preparation of LiOH/MPC ～

LiOH aq. (20 ml) + MPC (0.5 g)
→ Stirring (Magnetic stirrer: 600 rpm)
→ Filtration
→ Drying in vacuum dryer (150 °C, 15h)
→ **LiOH/MPC composite**

Table Preparation conditions

LiOH aq. Conc.	1, 5, 10 wt%
Stirring time	1, 24, 48 h

～ Measurement of hydration rate of composite ～

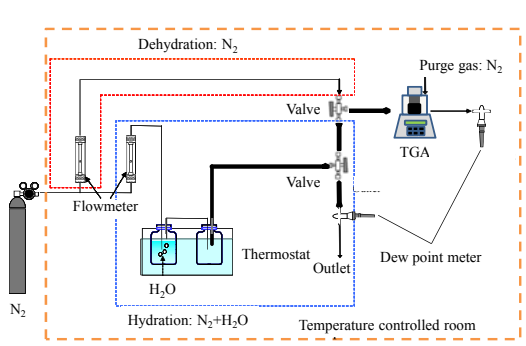


Fig. Schematic drawing of experimental apparatus

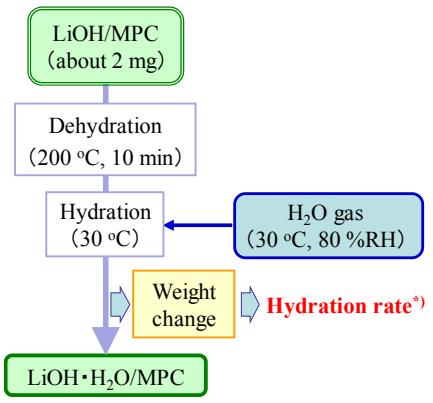


Fig. Procedure of hydration measurement

*) Hydration rate= Hydration rate of LiOH + Water adsorption rate of MPC

Results & Discussion

Demonstration of LiOH/MPC composite

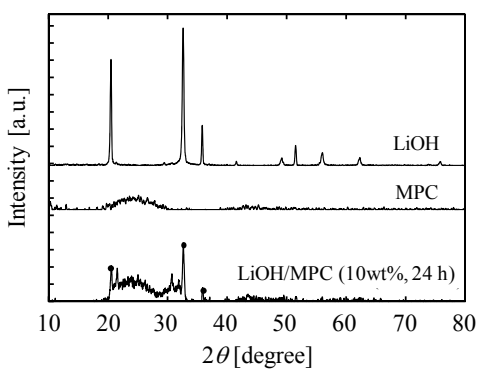


Fig. XRD patterns of LiOH, MPC and composite

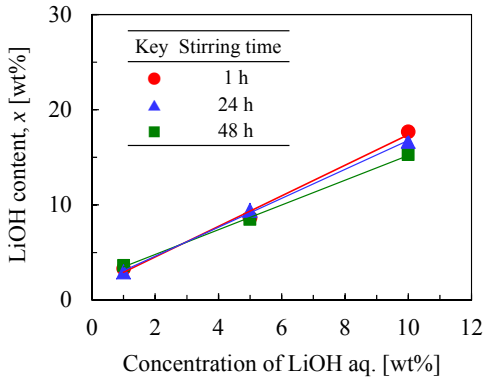


Fig. LiOH content in composite prepared at various concentrations of LiOH aq. & stirring time

✓ Diffraction peak of LiOH were observed for LiOH/MPC composite.
⇩
LiOH was deposited on the surface of MPC.

✓ LiOH content in composite linearly increased as increasing LiOH aq. concentration.
✓ LiOH content in composite was independent of stirring time.

Effect of LiOH content in composite on enhancement of hydration rate

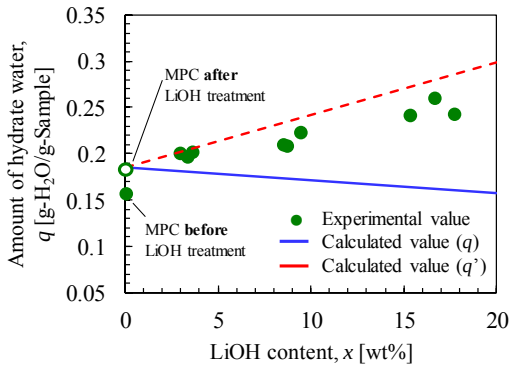


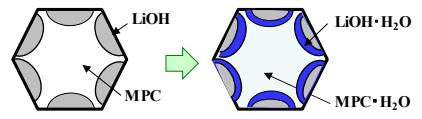
Fig. Effect of LiOH content on amount of hydrated water after 10 min hydration

$$q = q_{LiOH} \times (x/100) + q_{MPC} \times (1 - x/100)$$

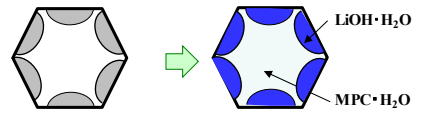
q : q_{LiOH} = 0.05 g-H_2O/g-LiOH @ 10 min (Hydration ratio: 6.6 %)

q': q_{LiOH} = 0.75 g-H_2O/g-LiOH @ 10 min (Hydration ratio: 100 %(Assumption))

***q* : LiOH, MPC absorbed $H_2O(g)$ independently.**



***q'* : Hydration of LiOH finished within 10 min.**



✓ Experimental value increased linearly as LiOH content in composite.
✓ Experimental value had a similar tendency to q'. (a little smaller than q')
⇩
LiOH almost completely reacted with water vapor within 10 min (?)

Hydration behaviors of LiOH/MPC composite

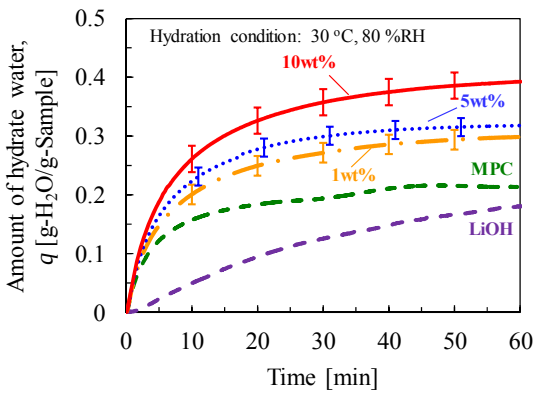


Fig. Time change in an amount of hydrated water of LiOH, MPC & composites

✓ **LiOH** : Hydration proceeded very **slowly**.
✓ **MPC** : Water adsorption occurred **rapidly**
⇩
An equilibrium state within 20 min.
✓ **Composite : Hydration rate was greatly enhanced.**
$q_{Composite} > q_{LiOH}$: 4.5 times @ 10 min.
$q_{Composite} > q_{MPC}$: 1.4 times @ 10 min.
⇩
Combination of LiOH & MPC is effective to enhance hydration of composite

✓ LiOH aq. concentration ↑
⇒ Hydration rate & hydrated water ↑

TEM image of LiOH/MPC composite

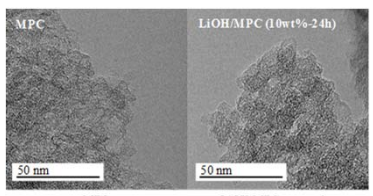


Fig. TEM images of MPC & composite

We imaged LiOH nanoparticles were deposited on the surface of MPC.
But….

✓ No difference between MPC and LiOH/MPC composite.
✓ LiOH nanoparticles could not be observed in the composite.

Li (light element) could not be detected by EDS.
⇒ **NaOH**/MPC composite was analyzed by EDS.

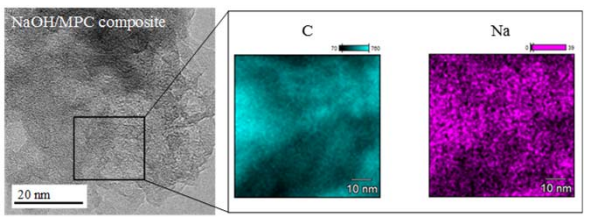


Fig. Carbon and Sodium mappings of NaOH/MPC composite by EDS

✓ Na has a similar distribution to C in NaOH/MPC.
✓ NaOH might be coated on the surface of MPC like a thin film

LiOH is also coated on the surface of MPC like **a thin film (?)**

Conclusion

- Hydration rate of LiOH is greatly enhanced by combining LiOH with MPC.
- LiOH/MPC composite prepared at LiOH aq. concentration of 10 wt% and stirring time of 24 hr achieved the highest hydration ratio after 10 min. hydration within this experimental conditions.
- Almost all LiOH in LiOH/MPC composite might react with water vapor within 10 min.
- From elemental mapping of composite, it is implied that LiOH is coated on the surface of MPC like thin film.

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