Hydrogen Storage Properties of Li-C-H system

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１．Introduction

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Reports on Carbon Materials as Hydrogen Storage Media

1997 A.C. Dillon et al., Nature, 386, 377
Storage of H_2 in single-walled carbon nanotubes

1999 P. Chen et al., Science, 285, 91
High H_2 Uptake by Alkali-Doped Carbon Nanotubes Under Ambient Pressure and Moderate Temp.

1999 Orimo et al., APL, 75, 3093
Hydrogen in the mechanically prepared nanostructured graphite

1. Introduction

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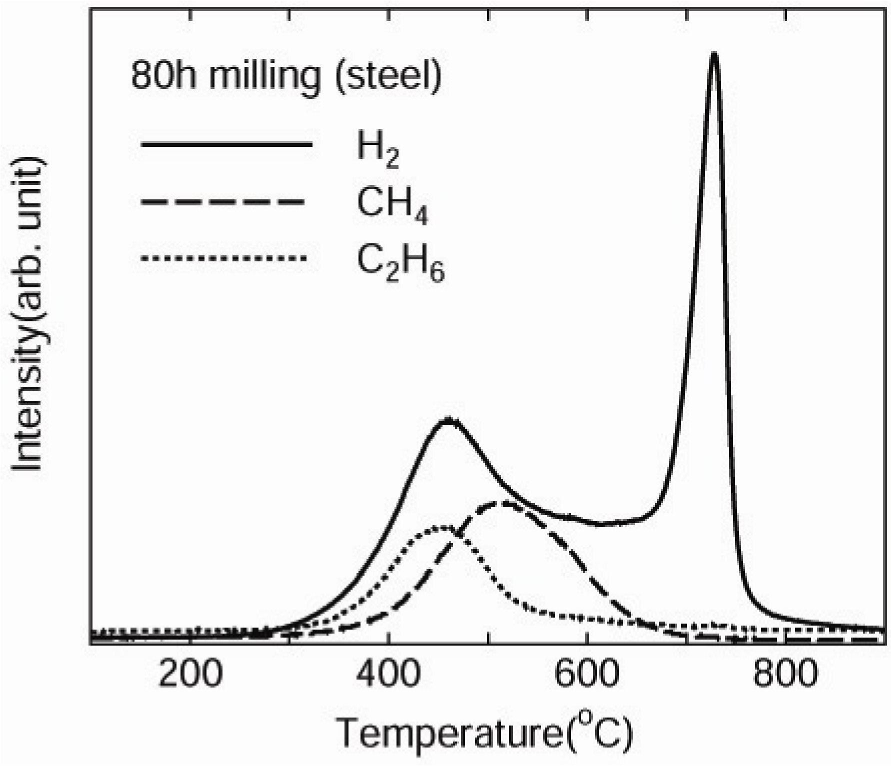
Hydrogenation of GRAPHITE by ball milling under H_2



- **H-storage capacity**
  : ~ 7 mass%
- Desorption gases
  : H_2, CH_4 C_2H_6, …
- Temperature range
  : 300℃ ~ 800℃

Orimo et al., APL, **75**, 3093

after the thermal desorption,
the sample CANNOT be rehydrogenated.

1. Introduction

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Planetary mill ＜Fritsch P7＞

Rocking mill ＜RM-10＞

C^nano H_x

Independent milling conditions

- ☆ **ball kind(Steel, ZrO_2)**
- ☆ **additives**
- ☆ **Atmospheres**
- ☆ **Milling time**
- ☆ **Milling type**

D.M. Chen, et al. J. Alloys Compd. **354**, (2003) L5
T. Ichikawa, et al. Mat. Sci. Eng. **B108**, (2004) 138
S. Isobe, et al. J. Phys. Chem. Sol. **65**, (2004) 535

１． Introduction

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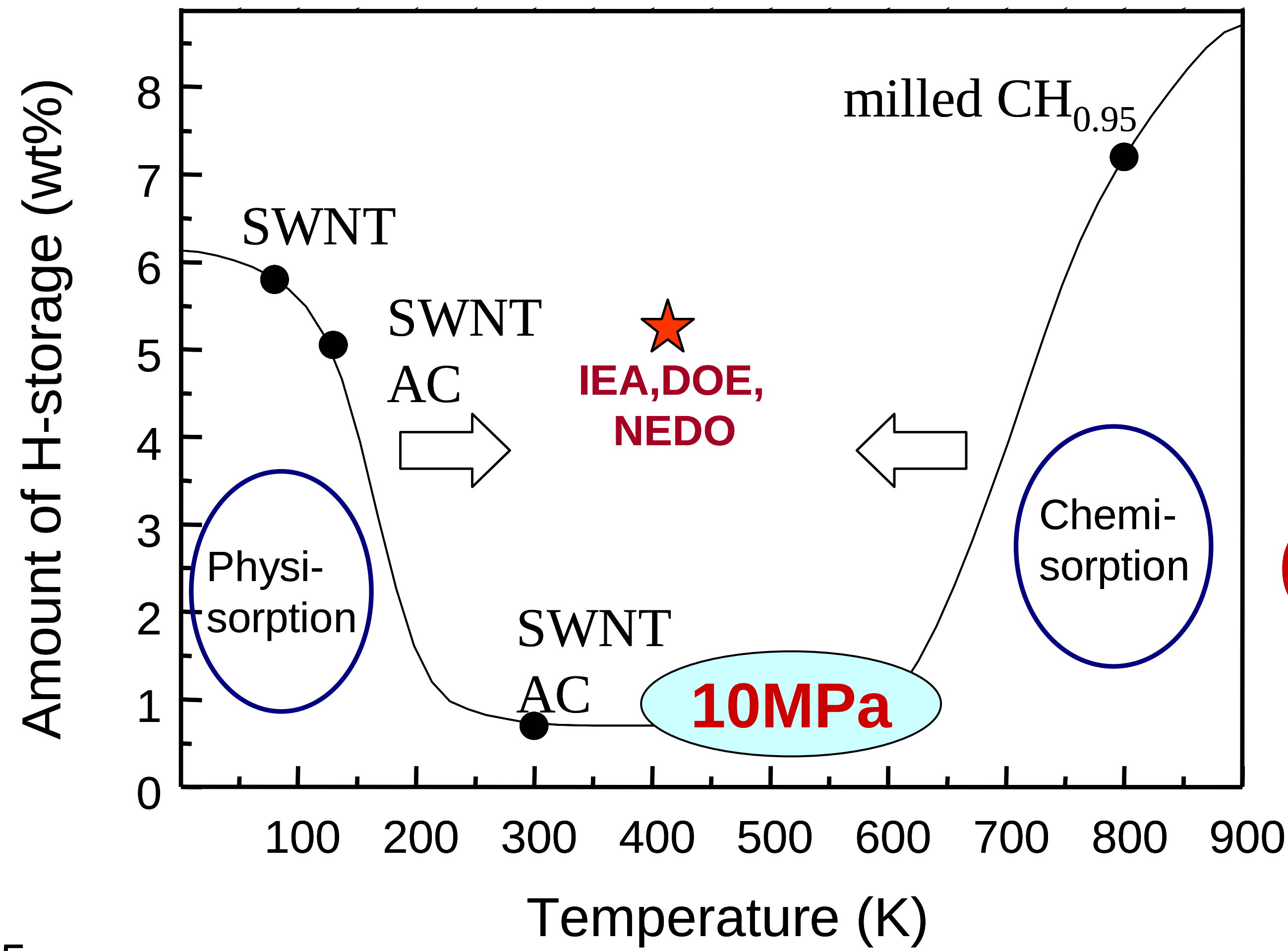
The relationship between H-Capacity and Working Temp. on carbon based materials

based on Hirscher et al. MH2004



for high capacity

Low Ｔemp.
（Physisorption）

or

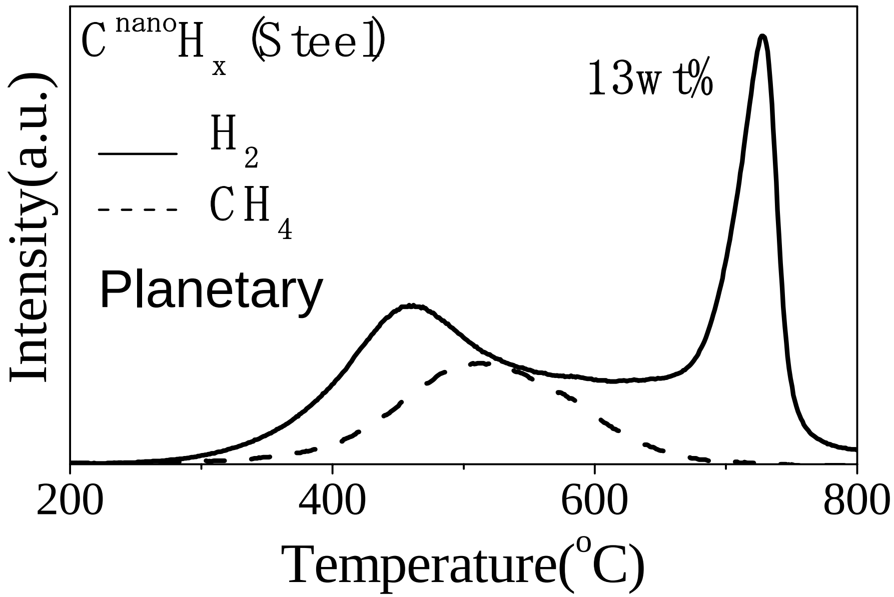
High Temp.
(Chemisorption)

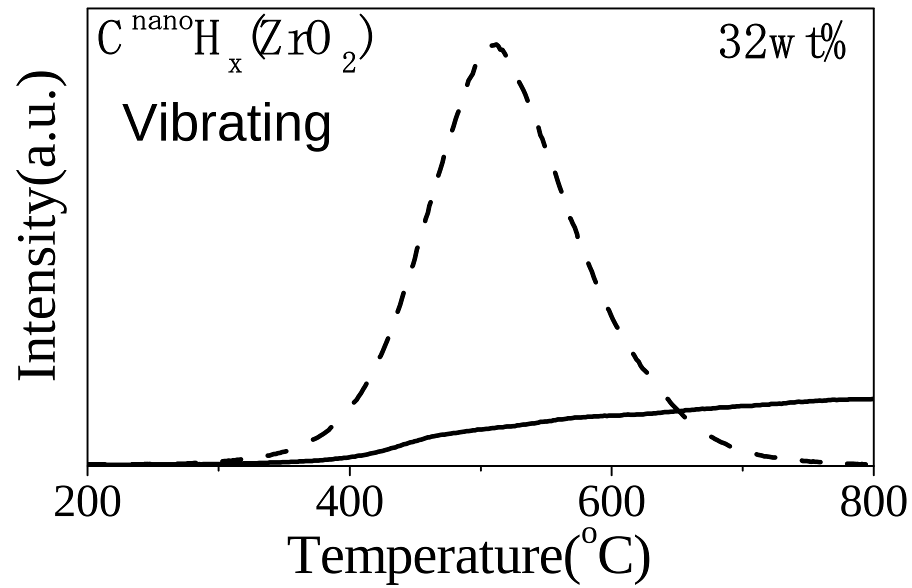
is necessary

2． Properties of $C^{nano}H_x$

Typical properties of $C^{nano}H_x$

Balls	Mill type	TG(900℃)	H-Desorption	H/C
Steel	Planetary	~ 15 wt%	2 peaks	~7wt%
ZrO_2			Single peak	~4wt%
Steel	Vibrating	~ 30 wt%	2 peaks	~7wt%
ZrO_2			Single peak	~4wt%





2． Properties of $C^{nano}H_x$

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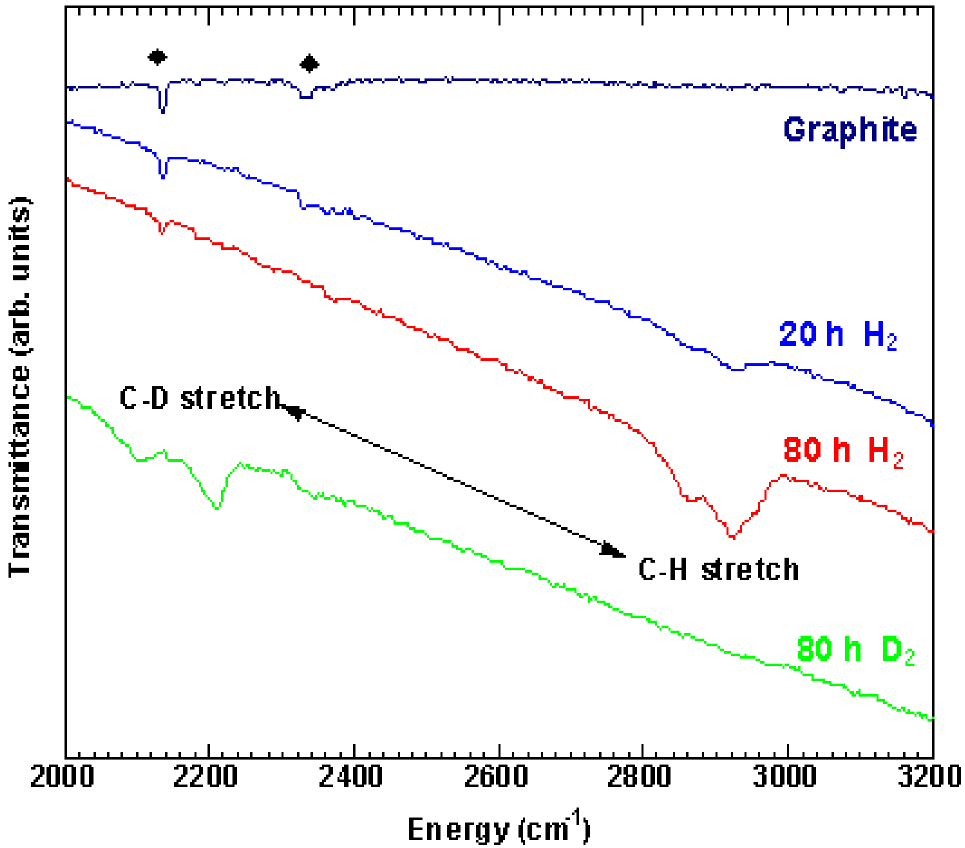
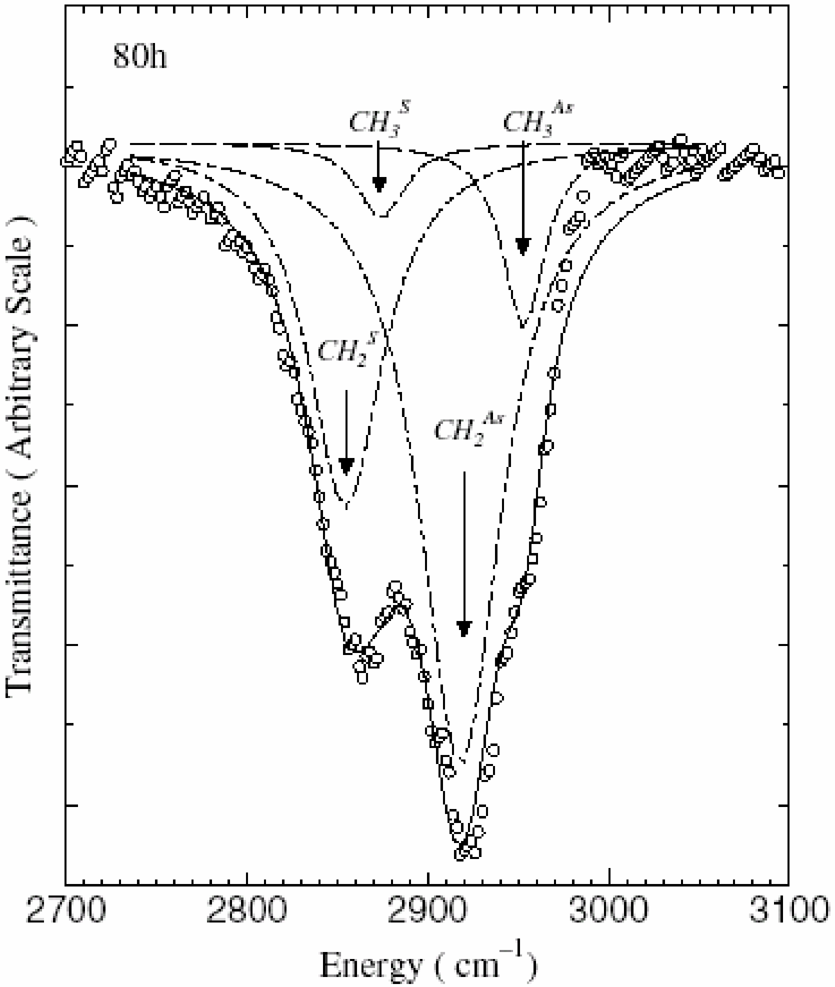
IR absorption profile





H atom can be absorbed as $-CH_3$ or $-C_2H_5$ in $C^{nano}H_x$

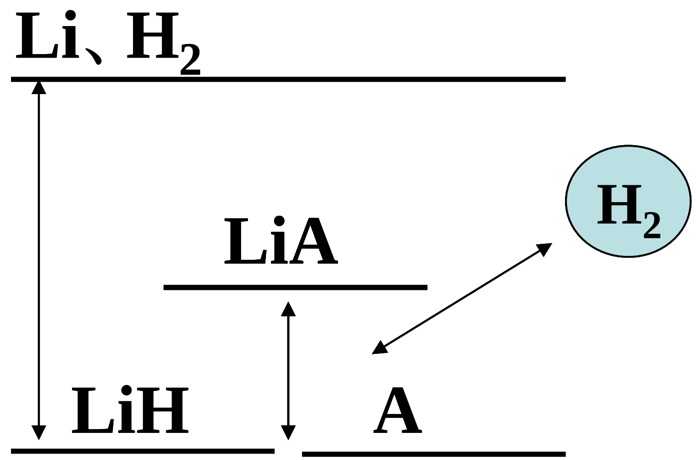
3． Solid-Solid Reactions with H_2 desorption

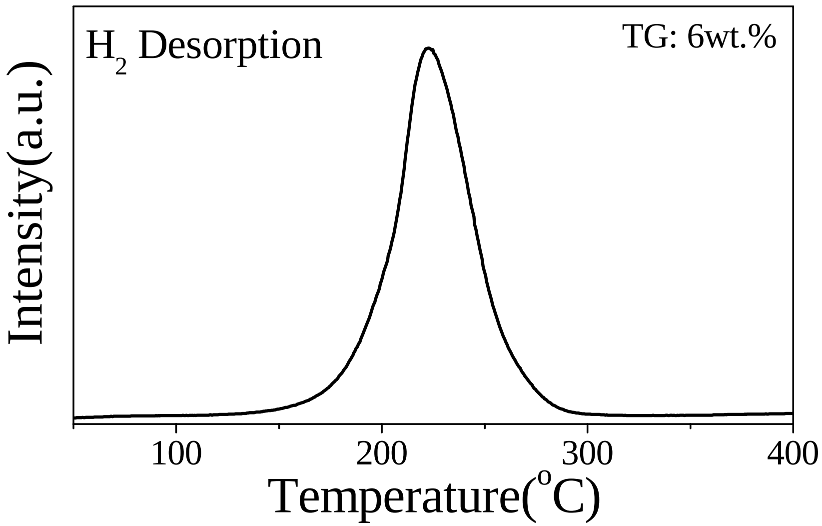
LiH： high H-Capacity (12.7mass%) BUT too stable……

HOWEVER….

$$LiH + LiNH_2 \Leftrightarrow Li_2NH + H_2$$

Solid-solid interaction can destabilize each other!





T. Ichikawa, et al. JALCOM **365**, (2004) 271
T. Ichikawa, et al. JPCB, **108**, (2004) 7887
H.Y. Leng, et al. JPCB, **108**, (2004) 8763
H.Y. Leng, et al. JPCB, **109**, (2005) 10744

３． Solid-Solid Reactions with H_2 desorption

Expected to destabilize both $C^{nano}H_x$ and LiH by making a ballmilled mixture

$C^{nano}H_x$ ： decompose above 300℃
on the edges of nano-carbon
: polarized material –CH_3, -CH_2

Destabilize

LiH ： decompose above 650ºC
very stable ***ion crystal***

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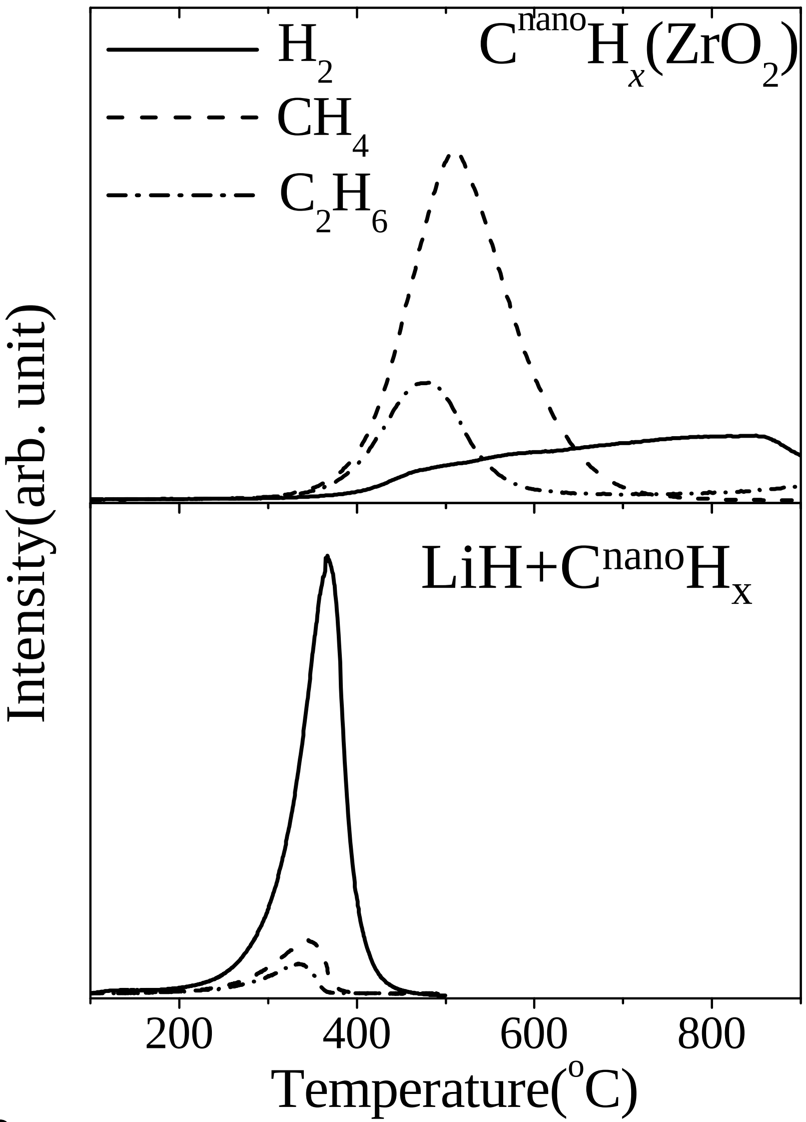
Destabilization of C-H by mixing with LiH



We have succeeded in destabilization of C-H bonding in CH_x^{nano} by mixing with LiH

a potential H-storage system

below 350 ℃

H-storage capacity: > 5 wt.%

A New Family of H-storage

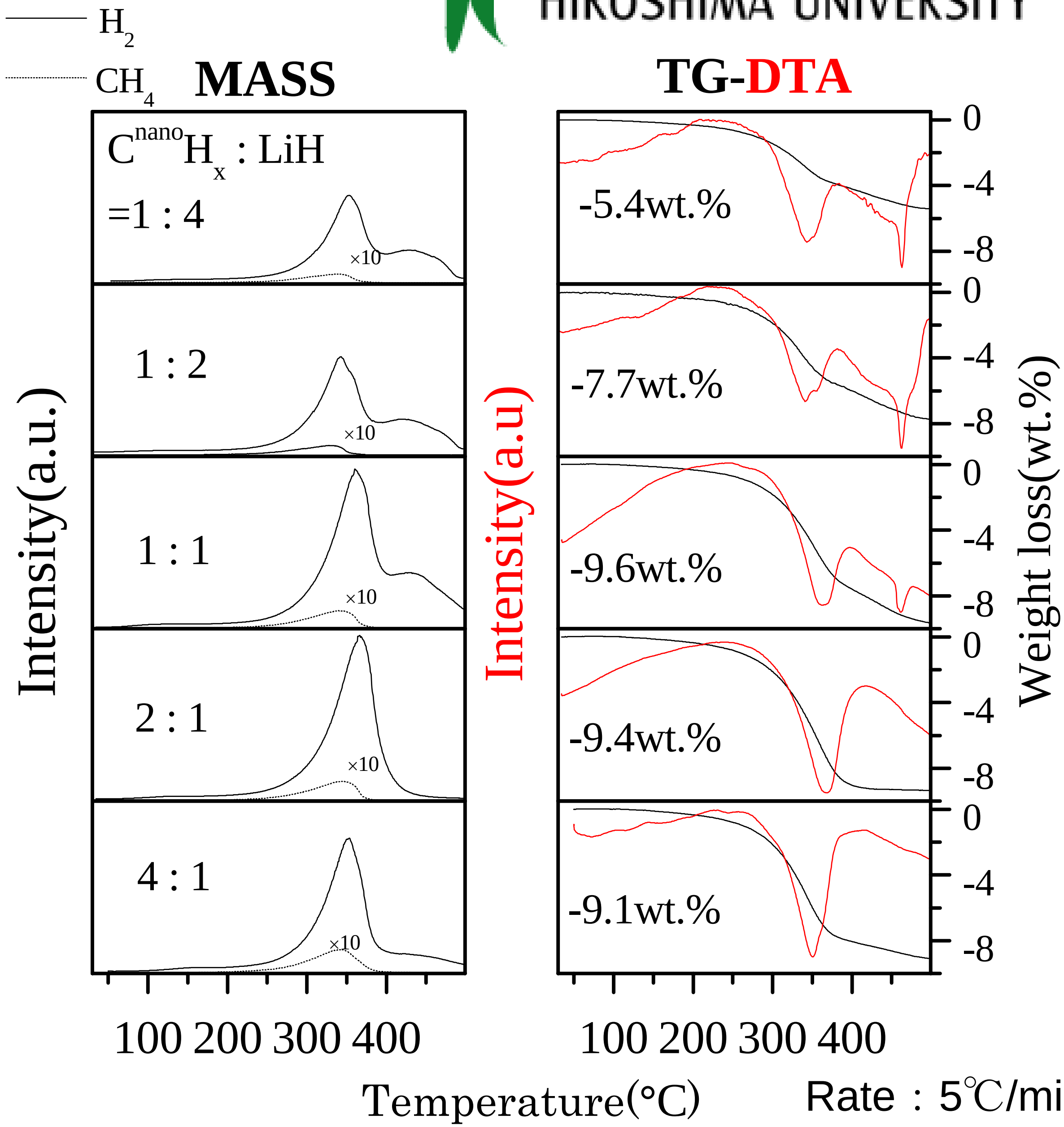
Li-C-H SYSTEM

T. Ichikawa, et al. APL, **86**, (2005) 241914

4. Li-C-H system

H-Desorption Properties
of different molar ratios
of LiH and $C^{nano}H_x$

- Lower $C^{nano}H_x$ ratio
  ⇒ lower weight loss
- Lower $C^{nano}H_x$ ratio
  ⇒ ***another reaction***
  at higher Temp.



Rate : 5℃/min

4. Li-C-H system

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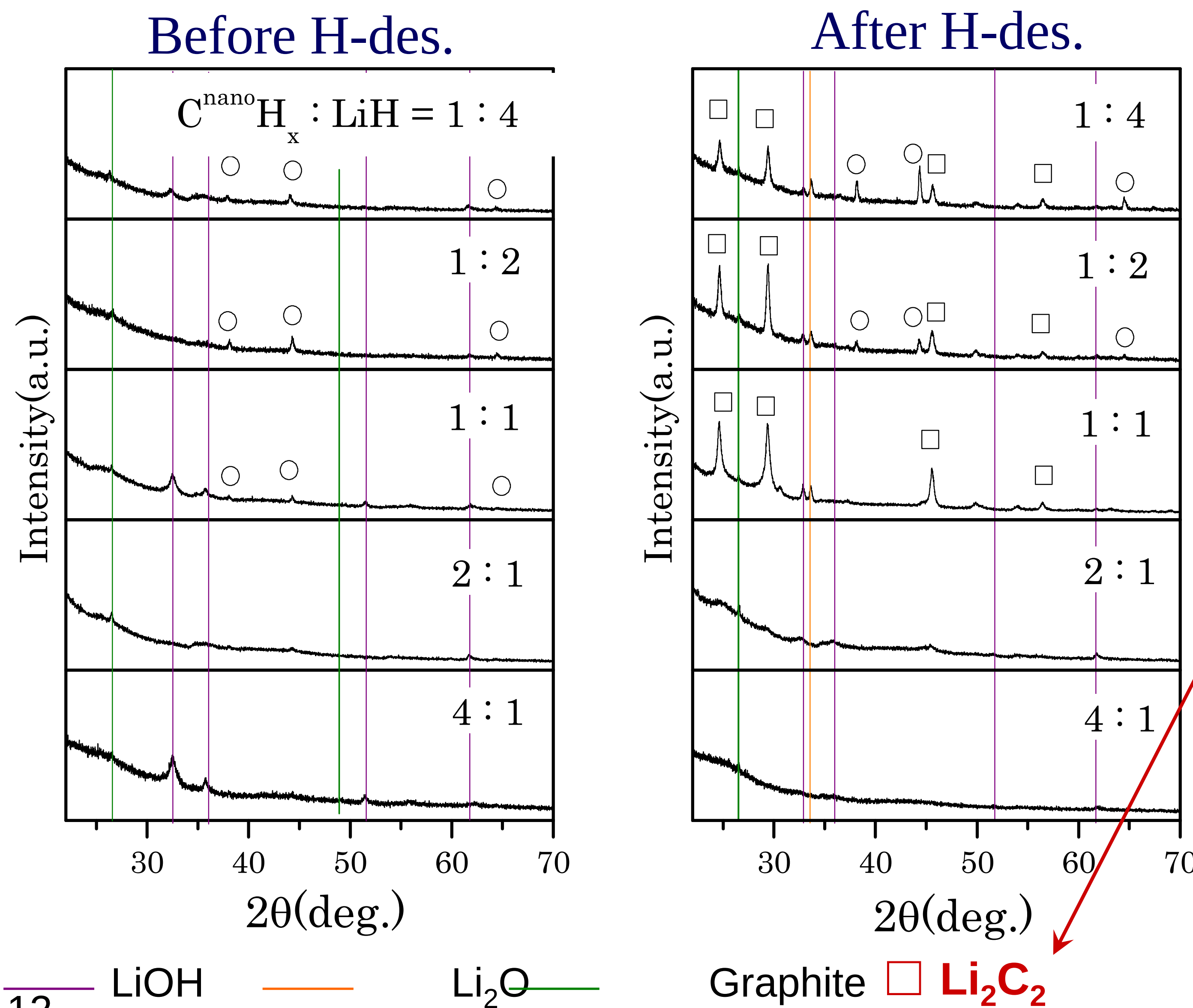
XRD Profiles



Typical character for LOWER $C^{nano}H_x$ ratio

Only these products can be rehydrogenated!

4． Li-C-H system

Cycle properties

Ball milled mixture
$C^{nano}H_x$: LiH=2:1

↓ **Start**

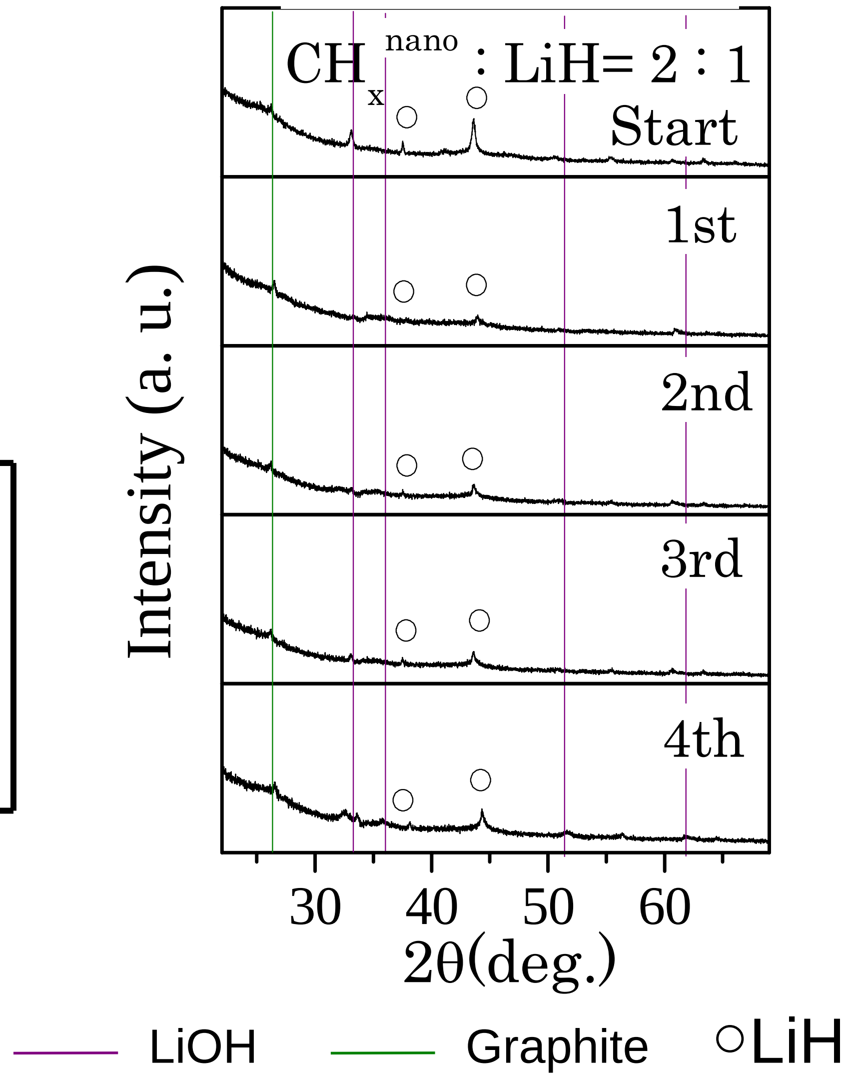
De-hydrogenation
at 350℃
for 8h under vacuum

↓

Re-hydrogenation
at 350℃ for 8h
under 3MPa H_2

1st ~ 4th

XRD profiles



4． Li-C-H system

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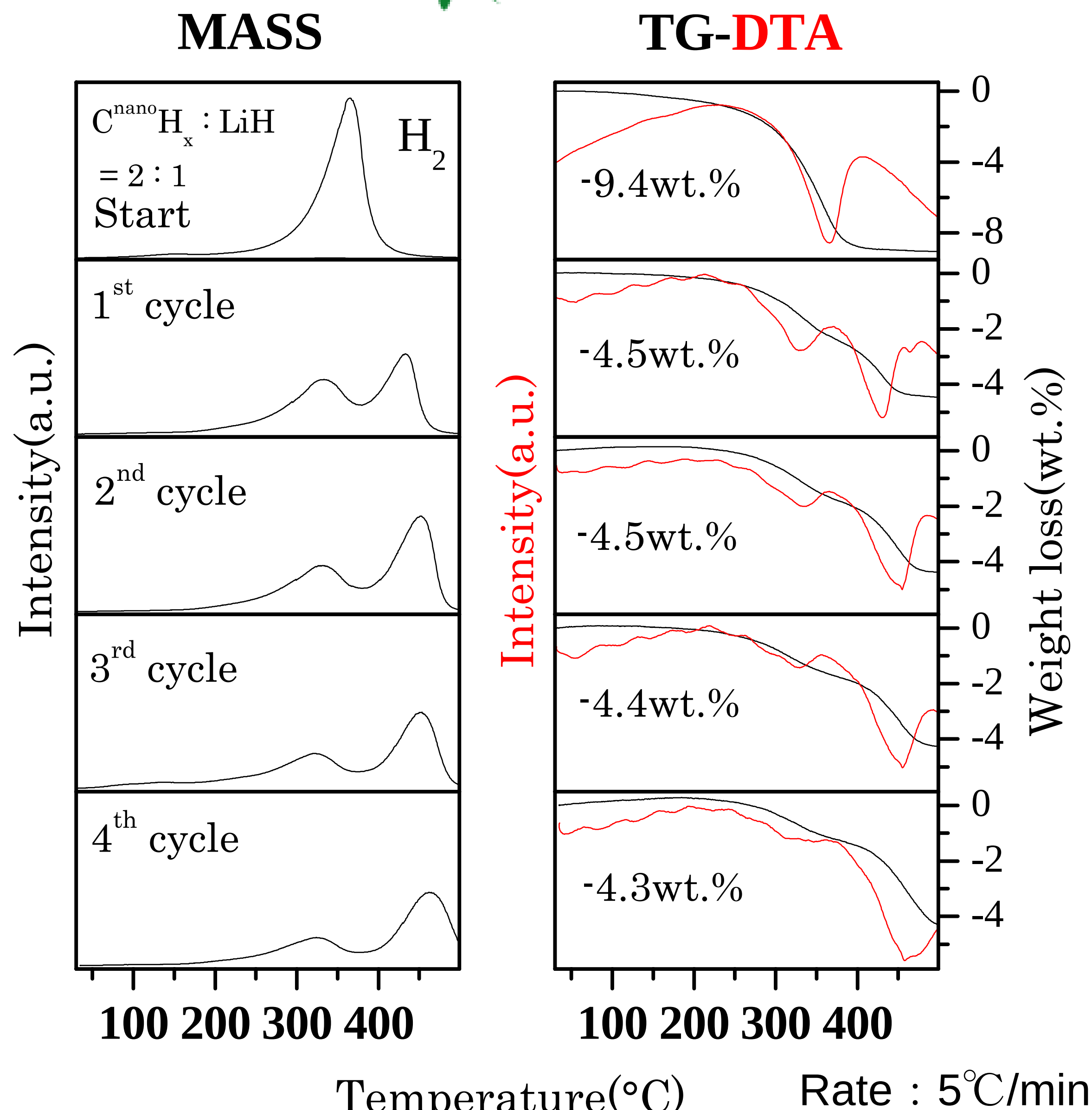
Cycle properties

- More than 4wt% H_2 can be reversibly stored in this product.
- The reaction mechanism should be clarified.
- The conditions must be optimized.



Rate : 5℃/min

5． Conclutions

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✓Novel Li-C-H system can REVERSIBLY store about 4.5wt.% H_2 around 350℃.

✓Lower $C^{nano}H_x$ ratio leads to crystallization of Li_2C_2, which shows worse H-storage properties.

✓The product with higher $C^{nano}H_x$ ratio keeps nano-structure during hydrogen desorptions and absorptions.

ACKNOWLEDGEMENT

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