The Hydrogen Storage Performance of Magnesium Based Nanostructures Prepared by Oblique Angle Deposition

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Outline:

- Introduction
- Hydrogenation behaviors
  1. Mg film versus Mg nanoblade array
  2. V decorated Mg nanoblade array
  3. Mg nanostructures with differently distributed V nanocatalysts
- Conclusions
Hydrogen Economy: Drivers

Fossil Fuels
- Potential exhaustion
- Pollution: CO, CO$_2$, SO$_2$, NO$_x$, dust
- Global warming

Hydrogen
- Abundant: 75% in universe; H$_2$O on earth as raw materials
- Clean: H$_2$+O$_2$ -> H$_2$O + energy
  Only produces energy and water, zero emission
- Renewable energy
Hydrogen Economy: Four Aspects

- **Hydrogen production**
  Today: Reform Fossil Fuels
  Tomorrow: Splitting H₂O

- **Hydrogen storage**
  Today: Gas and liquid
  Tomorrow: Solid state

- **Hydrogen transportation**

- **Hydrogen use**
  Today: Combustion \( H_2 \rightarrow \text{heat} \rightarrow \text{electricity} \)
  Tomorrow: Fuel cells \( H_2 \rightarrow \text{electricity} \)
Hydrogen Storage

Hydrogen storage is the bottleneck for hydrogen energy applications

- Pressurized gas
- Cryogenic liquid
- Solid-state storage
  - Metal hydrides
  - Complex hydrides
  - Carbon-based materials

Solid-state storage is the safest and most efficient method.
Revised Performance and Cost Targets

Performance targets revised in 2009 based on real-world experience with hydrogen fuel cell vehicles.

<table>
<thead>
<tr>
<th>Target</th>
<th>2015</th>
<th>2015</th>
<th>Ultimate*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>new</td>
<td>old</td>
<td>new</td>
</tr>
<tr>
<td>System Gravimetric Density [wt.%] (kWh/kg)</td>
<td>[5.5] (1.8)</td>
<td>[9] (3.0)</td>
<td>[7.5] (2.5)</td>
</tr>
<tr>
<td>System Volumetric Density [g/L] (kWh/L)</td>
<td>[40] (1.3)</td>
<td>[81] (2.7)</td>
<td>[70] (2.3)</td>
</tr>
<tr>
<td>System fill time for 5-kg fill [min] (kgH₂/min)</td>
<td>[3.3] (1.5)</td>
<td>[2.5] (2.0)</td>
<td>[2.5] (2.0)</td>
</tr>
<tr>
<td>System cost [$/kgH₂] ($/kWh_{ncl})</td>
<td>TBD</td>
<td></td>
<td>TBD</td>
</tr>
</tbody>
</table>

*Ultimate targets are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models.
Currently no technology is able to meet the revised 2015 targets.
New Ultimate targets remain very challenging.
Focus is on materials-based technologies that have potential to meet Ultimate targets and revised 2015.
Mg-Based Hydrogen Storage

MgH$_2$ is very promising for solid-state hydrogen storage

Advantages (Mg):
- Low cost
- Lightweight
- Nontoxic
- High hydrogen storage capacity: 7.6 wt% in MgH$_2$

Problem
- Poor hydrogen sorption thermodynamics and kinetics
  (MgH$_2$ is very stable, $T \geq 300^\circ$C is needed to release H$_2$)

Improvement
- Tailor Mg into nanostructures
- Add an appropriate transition metal catalyst
Tailor Mg into nanostructures

Conventional method: mechanical alloying or ball milling
Fabrication of Mg Film and Mg Nanoblade Array

Substrate

Mg Film
(nanoflakes)

Mg nanoblade array

Substrate

Film

Source

Normal deposition

Source

Oblique angle deposition (OAD)

Hydrogenation (PCT Pro-2000):
20 bar H-pressure
2000 minutes
200°C, 250°C, 300°C, 350°C

He et al., APL 2008, 93, 163114.
Fabrication and Characterization Systems
Hydrogenation at Different Temperatures

**Mg Thin Film**

- Sample height $h \approx 4 \mu m$

**Mg Nanoblades**

- $(a)$ A
- $(b)$ A300
- $(c)$ A350

- $(d)$ B
- $(e)$ B300
- $(f)$ B350

- $h \approx 7.1 \mu m$
- $t \approx 160 nm$
- $\eta \approx 41\%$

- $h \approx 7.3 \mu m$
- $t \approx 220 nm$
- $\eta \approx 69\%$

- $h \approx 7.7 \mu m$
- $t \approx 250 nm$
- $\eta \approx 69\%$

He et al., APL 2008, 93, 163114.
Hydrogenation at Different Temperatures

He et al., APL 2008, 93, 163114.
FRES (Forward REcoil Spectrometry)

(a) Film

(b) Nanobrade array

He et al., APL 2008, 93, 163114.
FRES (Forward REcoil Spectrometry)

- $T \approx 250^\circ C$ (blades) vs $T \approx 350^\circ C$ (film)
- MgO $\rightarrow$ small H amount in blades
- The unique nanoblade morphology and catalysis of Ti layer $\rightarrow$ nanoblade hydrogenation behavior.

He et al., APL 2008, 93, 163114.
Add an appropriate transition metal catalyst
Fabrication of V-Decorated Mg Nanoblade Arrays

He et al., Nanotechnology 2009, 20, 204008.
Fabrication of V-Decorated Mg Nanoblade Arrays

He et al., Nanotechnology 2009, 20, 204008.
Characterizations: SEM and EDX

Scale bars: 5 μm

Mg vapor

$h \approx 50 \mu m$
$t \approx 65 nm$

Intensity (a.u.)

V/(Mg+V) \approx 2.25 \text{ at.}\%$

He et al., Nanotechnology 2009, 20, 204008.
Hydrogen Storage Performance

Kinetic curves

(a) H-absorption (wt.%) under vacuum
(b) H-desorption (wt.%) under 10 bar H₂

He et al., Nanotechnology 2009, 20, 204008.
Hydrogen Storage Performance

Spherical particle (radius $R$) model

$$\frac{\partial C_H}{\partial t} = -k_H C_H + D_H \nabla^2 C_H$$

$$\begin{cases} C_H(r < R, t = 0) = C_0 & \text{Initial condition} \\ C_H(r = R, t > 0) = C_s & \text{boundary condition} \end{cases}$$

$$\frac{C_H - C_0}{C_s - C_0} = 1 + \frac{2R}{\pi r} \sum_{m=1}^{\infty} \frac{(-1)^n}{m} \sin \frac{m\pi r}{R} \exp\left[-\left(\frac{D_H m^2 \pi^2}{R^2} + k_H\right)t\right]$$

The larger $k_H$ & $D_H$, and smaller $R$, the faster the kinetics

- The V coating
- The unique nanoblade morphology:
  1. large surface area
  2. small H-diffusion length.

He et al., Nanotechnology 2009, 20, 204008.
Mg nanostructures with differently distributed V nanocatalysts

He et al., Int J Hydrogen Energy 2010, 35, 4162
Fabrication of V-Decorated Mg Nanoblade Arrays

He et al., Nanotechnology 2009, 20, 204008.
Fabrication of V-Incorporated Mg Nanostructures

V decorated Mg at 70°

V doped Mg at 10°, 50°, 70°

He et al., Int J Hydrogen Energy 2010, 35, 4162
Morphological Characterizations

V decorated Mg at 70°
As-prepared

V doped Mg at 70°
As-prepared

V doped Mg at 50°
As-prepared

V-Mg

Ti rods
Ti film
Si

(a) 10 μm
(b) 2 μm
(c) 2 μm
(d) 2 μm

(a′) 10 μm
(b′) 2 μm
(d) 2 μm

After 14 cycles
After 21 cycles
As-prepared

4.6 at% V
He et al., Int J Hydrogen Energy 2010, 35, 4162
TEM and ED (As-Prepared Samples)

V decorated Mg at 70°:
- V crystals in Mg matrix
- Rings (V) + spots (Mg) in ED

V doped Mg at 70°:
- No V signal is detected
- Only Mg diffraction spots in ED

He et al., Int J Hydrogen Energy 2010, 35, 4162
Hydrogen Storage Performance

He et al., Int J Hydrogen Energy 2010, 35, 4162
Progress: Material Capacity vs. Temperature

Open symbols denote new mail's for FY2009

New DOE system targets

Material capacity must exceed system targets

Solid AB (NH₃BH₃)

Metal hydrides

Chemical hydrides

Sorbents

IRMOF-177

PCN-12
C aerogel

Carbide-derived C

BIC
MOF-74

Li₂Zr(BH₄)ₓ

Na₂Mn(BH₄)₂

NaAlH₄

NaMn(BH₄)₂

PANI

H₂ sorption temperature (°C)

Temperature for observed H₂ release (°C)
Conclusions

The H-storage performance of Mg can be improved by

1. Tailoring Mg into nanoblades
2. Coating a layer of V on the surface of individual Mg nanoblades

The H-storage performance of V-Mg depends strongly on the distribution of V nanocatalyst
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