Fueling the Future: High-Density Hydrogen Storage in Hybrid Nanomaterials

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The Importance of Hydrogen as an Energy Carrier

How will we fuel ourselves in the future?

Historical trend toward decarbonization is clear

- Not quite the Carbon equivalent of “Moore’s Law”:
- H$_2$ generation, storage, distribution all imperfect at present

Why Hydrogen?

Hydrogen has a high energy density, it is abundant, and \( \text{H}_2\text{O} \) is the sole combustion product.

The “big 8” major auto manufacturers (BMW, Toyota, Honda, Hyundai, etc) have committed to Hydrogen FCEVs.

**Major OEM Activities and Plans for FCEVs**

- Ford, Daimler AG, and Renault-Nissan announced a partnership to speed up the development of zero-emission fuel cell electric vehicles by sharing the costs of investment.
- BMW and Toyota are close to finalizing a deal for the future of each automaker’s hydrogen fuel cell technology.

- **Toyota**
  - 2010-2013: U.S. demo fleet of 100 vehicles
  - 2015: Target for large-scale commercialization
  - “FCHV-adv” has achieved 431-mile range and 68 mpgge

- **Honda**
  - Clarity FCX named “World Green Car of the Year”; EPA certified 72mpgge; leasing up to 200 vehicles
  - 2015: Target for large-scale commercialization
  - Small-series production of FCEVs began in 2009
  - Plans for tens of thousands of FCEVs per year in 2015 – 2017 and hundreds of thousands a few years after
  - In partnership with Linde to develop fueling stations
  - Recently moved up commercialization plans to 2014

- **Daimler**
  - FCEVs are key part of “Nissan Green Program”

- **General Motors**
  - 115 vehicles in demonstration fleet
  - 2012: Technology readiness goal for FC powertrain
  - 2015: Target for commercialization

- **Hyundai-Kia**
  - 2012-2013: 2000 FCEVs/year; 2015: 10,000 FCEVs/year
  - “Borrego” FCEV has achieved >340-mile range

- **VW**
  - Expanded demo fleet to 24 FCEVs in CA
  - Recently reconfirmed commitment to FCEVs

- **BMW**
  - Planning potential partnership with CA on FCEVs

\* In 2009, several major auto manufacturers signed a letter of understanding anticipating widespread commercialization of FCEVs beginning in 2015 and calling for increased investment in \( \text{H}_2 \) infrastructure (Ford and Renault not shown here).

**Gravimetric Energy Density**

- Hydrogen: 143 kJ/g
- Methane: 56 kJ/g
- Gasoline: 49 kJ/g
- Coal: 24 kJ/g

Based on publicly available information in 2011-2012.
Challenges to Efficient Gas Storage

Notable properties of Magnesium (Mg):

- Environmental friendliness, low cost, earth abundant
- High H$_2$ gravimetric density (7.6 wt%) (DOE 2017 Target is 5.5 wt%)
- High bond formation enthalpy. Temperatures of 350 - 400 °C needed.
- Poor kinetics, oxidative instability

4kg H$_2$ ~250 mi.

Nature 2001, 414, 353
Designing Optimum Hydrogen Storage Materials

Target system is hybrid material:
Mg nanocrystals in a gas-selective matrix

System Advantages
- high storage capacity of Mg (7.6 wt %)
- many potential routes to enhance kinetics
- air-stable and injectable/moldable
- robust to size-changes from cycling
New Platform: Air-Stable Mg-PMMA Composites

Poly(methyl methacrylate) (PMMA) H₂/O₂ permeability: 42.9

Nature Materials 2011, 10, 286-290
Energy Environ. Sci., 2013, 6, 3267–3271
Storage and Stability in Mg-PMMA Composites

- Metal-hydride polymer nanocomposites can be a new platform for stable and high-performance gas storage.

*Nature Materials 2011, 10, 286-290*
Remarkable dual enhancement drives up both loading and stability! Now absorbing over 90% of theoretical maximum for Mg metal.
Counter-Intuitive Optimization: 
More Nanocrystals, Less Oxidation

Increasing % Mg

Energy Environ. Sci., 2013, 6, 3267–3271
Why Loading Inversely Correlates with Permeability

1. Increased tortuosity: particles now packed more densely than mfp of gas

2. Morphological changes: Polymer-NP interactions rigidify polymer, reduce chain mobility

Model: volume fraction > 42% polymer chain motion dominated by interaction with NPs

Enhancing the Kinetics of H\textsubscript{2} Sorption

Capacity and stability are necessary, but not sufficient

- DOE targets: operating range: -40/60 °C, refill time of 3.3 min

Approach: Catalyst dopants

- Enhance dissociation of H\textsubscript{2} for better absorption, improved diffusion in hydrided phase
Mg Nanocrystal Doping: $H_2$ Sorption Accelerated

- Small amount of dopant (5 wt% per Mg) has dramatic impact on kinetics – now meeting kinetic filling targets...

Ruminski et al. *in preparation*
# Mg Doping: Enhancing Kinetics of H2 Sorption

## Absorption

<table>
<thead>
<tr>
<th></th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/mol K)</th>
<th>Ea (kJ/mol)</th>
<th>P_{eq} @ 300 °C (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg - bulk</td>
<td>-74.6</td>
<td>-135</td>
<td>95-130</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>-34.1</td>
<td>-62.6</td>
<td>99.7</td>
<td>2.5</td>
</tr>
<tr>
<td>Mg-X</td>
<td>-34.2</td>
<td>-62.3</td>
<td>83.5</td>
<td>2.4</td>
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</table>

### Shift in $P_{eq}$ increases driving force

## Desorption

<table>
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<tr>
<th></th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/mol K)</th>
<th>Ea (kJ/mol)</th>
<th>P_{eq} @ 300 °C (bar)</th>
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<tbody>
<tr>
<td>Mg - bulk</td>
<td>75</td>
<td>130</td>
<td>120-160</td>
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<tr>
<td>Mg</td>
<td>35.5</td>
<td>63.4</td>
<td>TBD</td>
<td>1.4</td>
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<tr>
<td>Mg-X</td>
<td>33.8</td>
<td>60.7</td>
<td>83.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Toward the Atomic Limit for Separations: Graphene Layers as Gas Barrier

Graphene Oxide (GO) as a selective hydrogen barrier layer

- GO layers exhibit high mixed gas separation selectivities: 3400 (for $\text{H}_2/\text{CO}_2$ mix) and 900 (for $\text{H}_2/\text{N}_2$ mixtures)
Multilaminate “Ravioli” of Reduced Graphene Oxide (rGO) and Mg Nanocrystals

After synthesis

After 3 months air-exposure

Intensity (a.u.)

$\text{Mg}$

$\text{MgH}_2$

$\text{Mg(OH)}_2$

$\text{MgO}$

E.S. Cho et al, submitted
Hydrogen Absorption & Desorption in rGO-Mg

Absorption at 200°C & 15 bar
Desorption at 300°C & 0 bar

- The Mg NCs absorb 7.3 wt% H2 in Mg (theoretically 7.6wt%)
- H2 sorption is 6.3 wt% for total composite (beyond FCEV target- 5.5%)!

E.S.Cho et al, submitted
Cycling and Temperature Dependence

Cyclability and lower temperature performance are key metrics

Multilaminate composite shows good cycle-ability and promise for low T

E.S.Cho et al, *submitted*
Stability of Composite: Metallic Nano-Mg Air-Robust

The composite shows a combination of Mg and MgH$_2$ after cycling, and excellent air stability.
Raman Spectroscopy on rGO-Mg Laminates

- D peak corresponds to defect sites and related to sp² domain size; the G peak originates from sp² C=C, and 2D peak provides information on the number of layers of graphene.
- I(D)/I(G) is increased after synthesis, consistent with GO reduction

E.S. Cho et al, submitted
In-Situ Methodology for Nanoscale Phase Transitions

- First direct imaging of in-situ hydriding phase transitions
- Developed new framework for nanoconfinement on reactive transformations
- Implications for catalysis, batteries, etc.

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