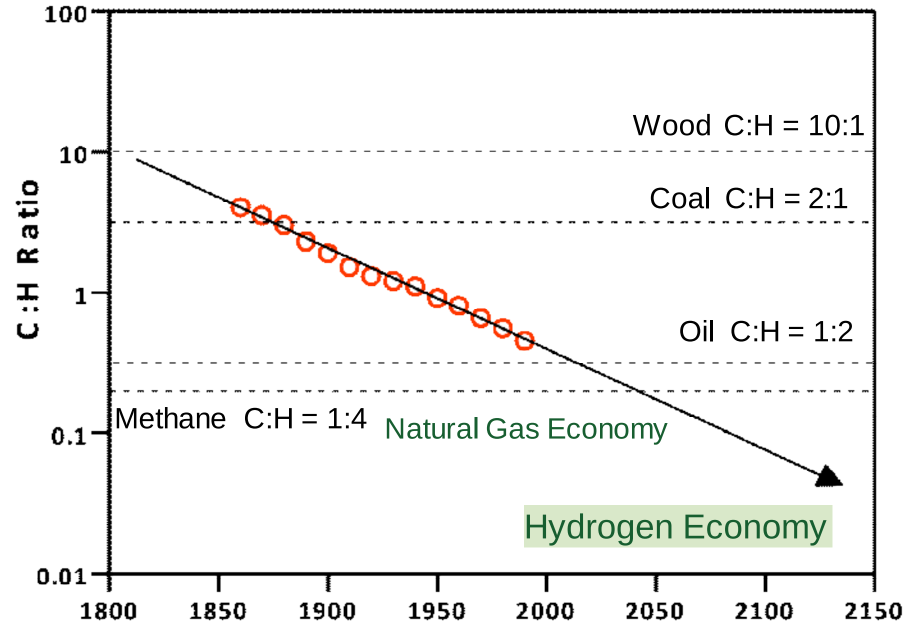
Fueling the Future: High-Density Hydrogen Storage in Hybrid Nanomaterials

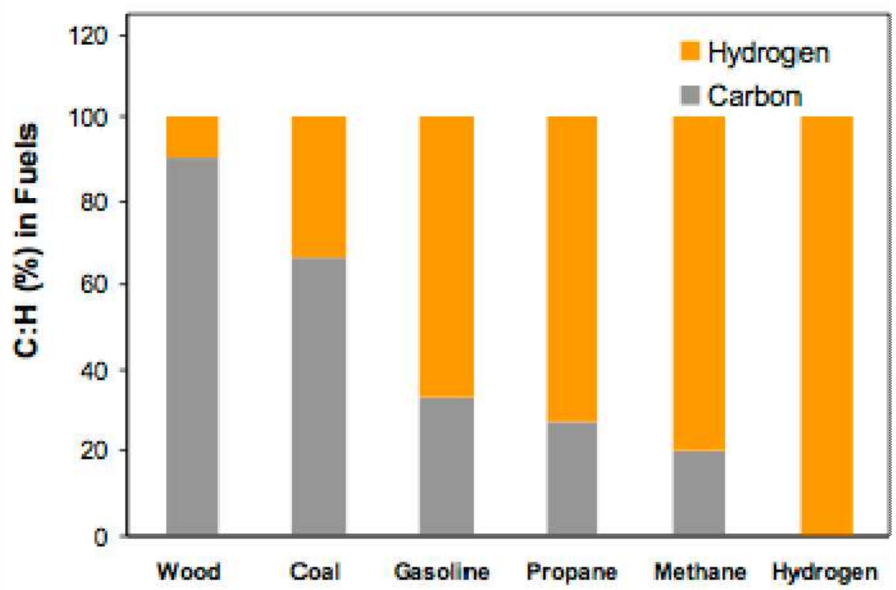
NCCAVS TFUG Meeting
September 22, 2014

Jeff Urban
The Molecular Foundry, Berkeley Labs
foundry.lbl.gov

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

Molecular Foundry

IIASA, BP (1965-2001), CDIAC, Ausabel (2007)

BERKELEY LAB

Why Hydrogen?

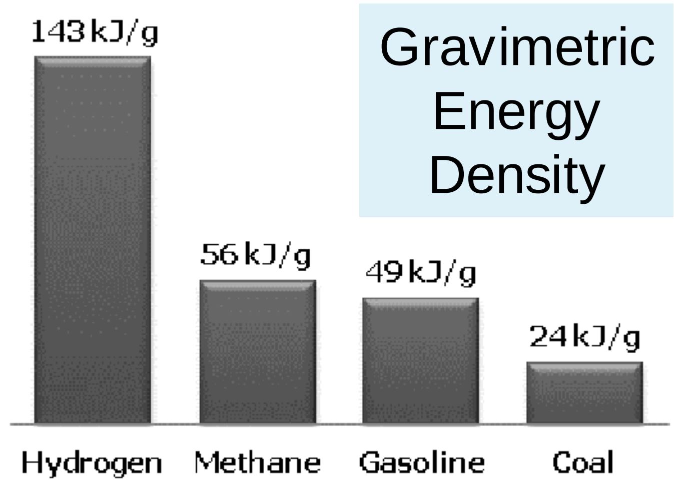
Major OEM Activities and Plans for FCEVs

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
Daimler*	• 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*
Nissan*	• 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 GM 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 H_2 infrastructure (Ford and Renault not shown here).*

Based on publicly available information in 2011-2012.



Hydrogen has a high energy density, it is abundant, and H_2O is the sole combustion product

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

Molecular Foundry

from energy.gov

BERKELEY LAB

Challenges to Efficient Gas Storage

Nature **2001**, 414, 353

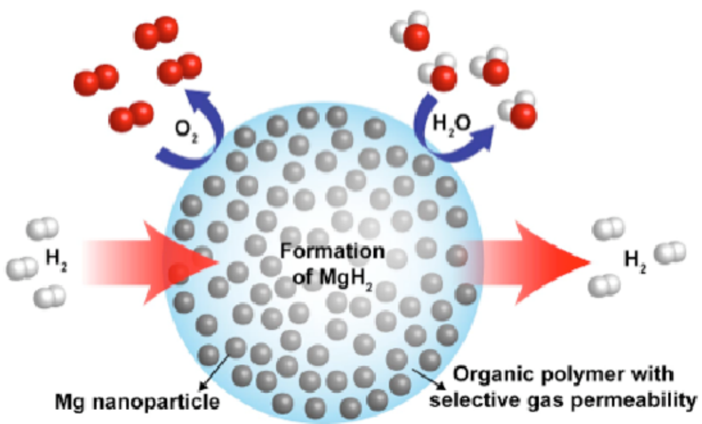
Notable properties of Magnesium (Mg):

- 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

Designing Optimum Hydrogen Storage Materials

Storage Density	Storage Kinetics	Air-Stability
Metal hydride	Nanoscale Material	Gas-Selective Matrix

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



System Advantages

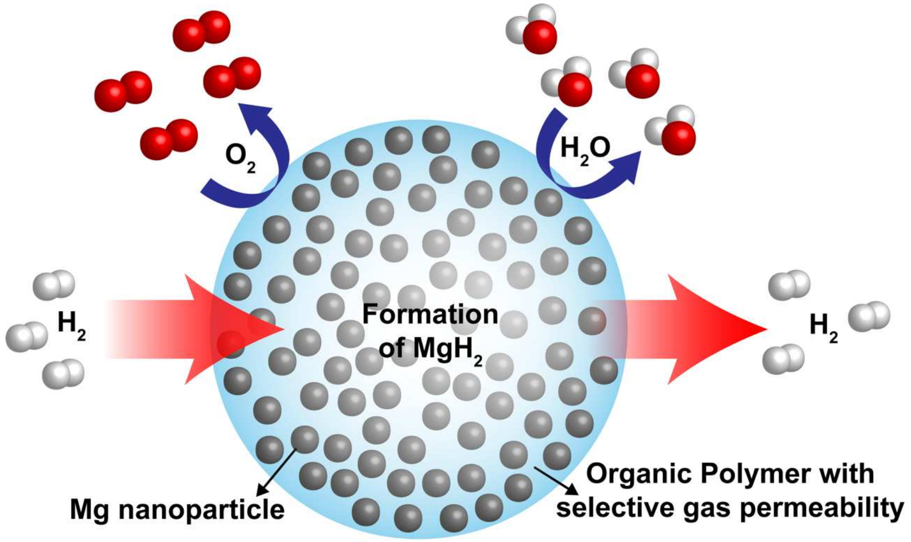
- high storage capacity of Mg (7.6 wt %)
- many potential routes to enhance kinetics
- air-stable and injectable/moldable
- robust to size-changes from cycling

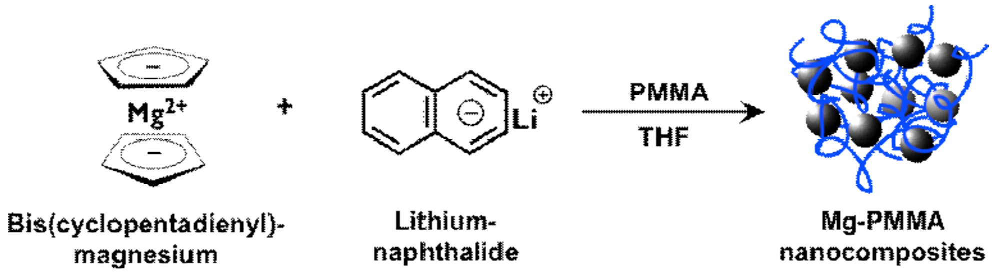
Molecular Foundry

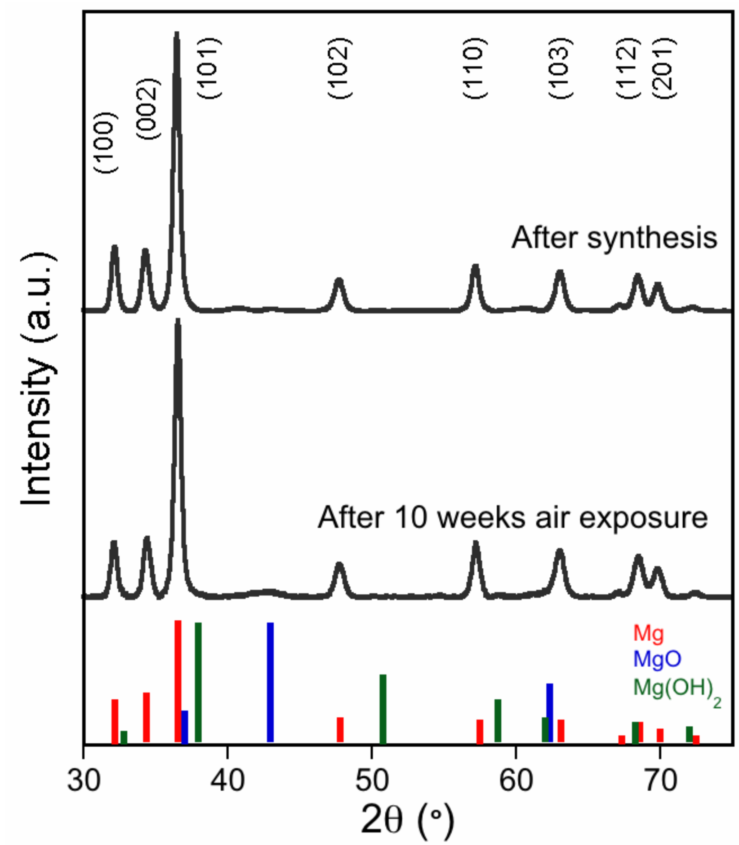
BERKELEY LAB

New Platform: Air-Stable Mg-PMMA Composites

Poly(methyl methacrylate) (PMMA)
H_2/O_2 permeability: 42.9







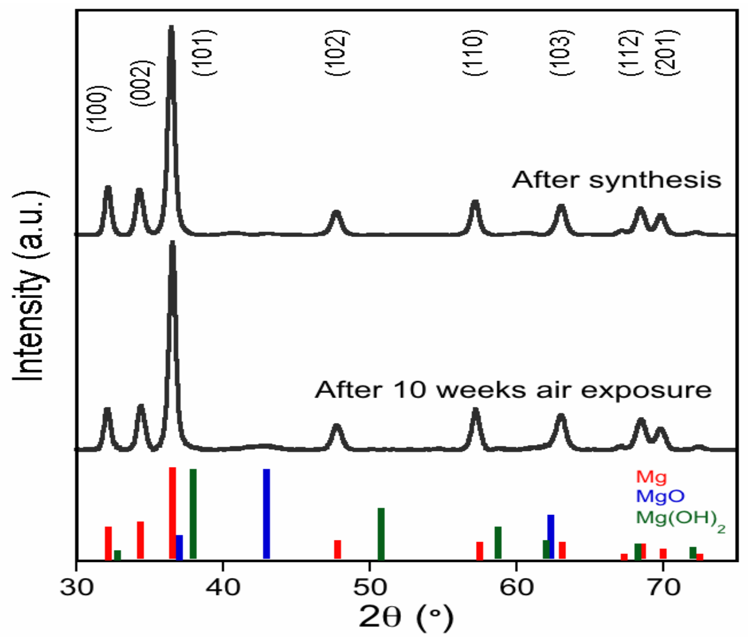
Nature Materials **2011**, 10, 286-290

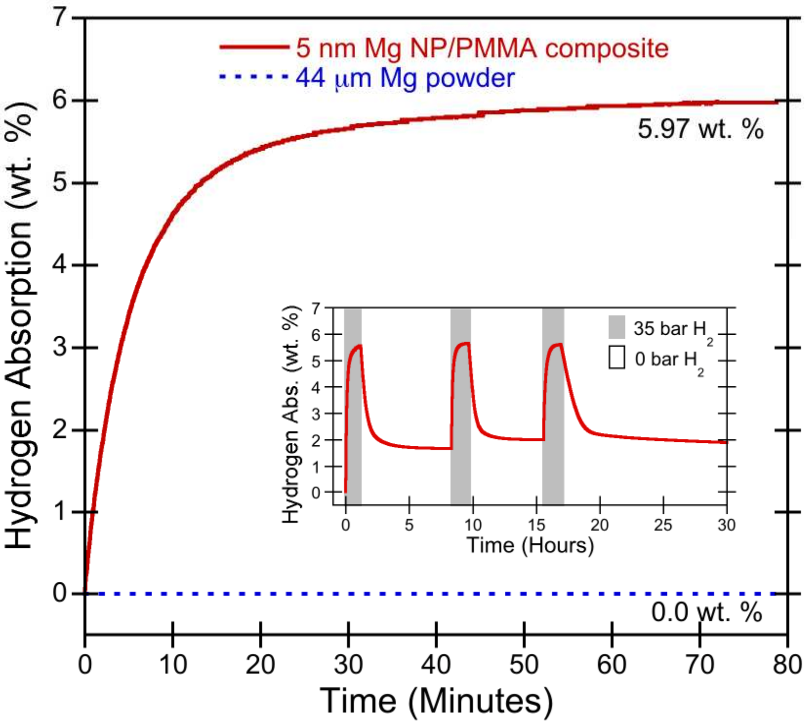
Energy Environ. Sci., **2013**, 6, 3267–3271

Molecular Foundry

BERKELEY LAB

Storage and Stability in Mg-PMMA Composites



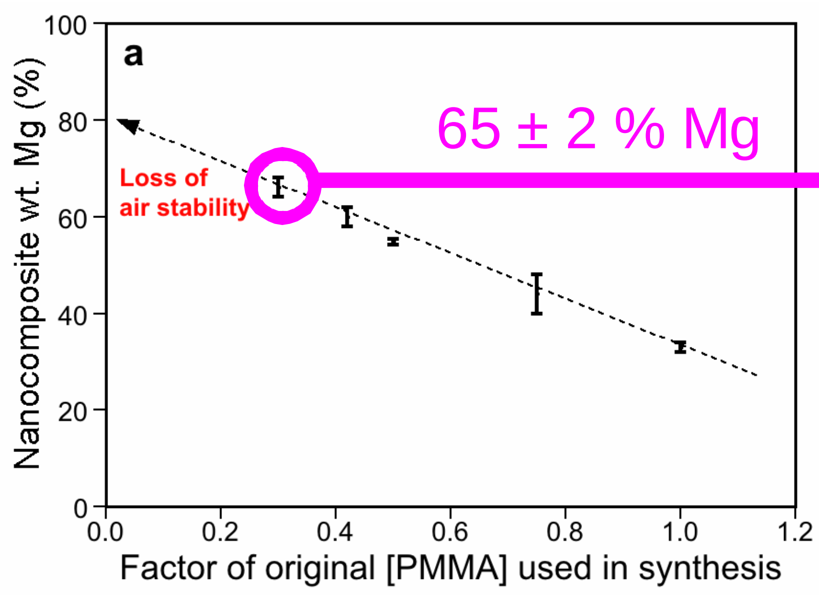


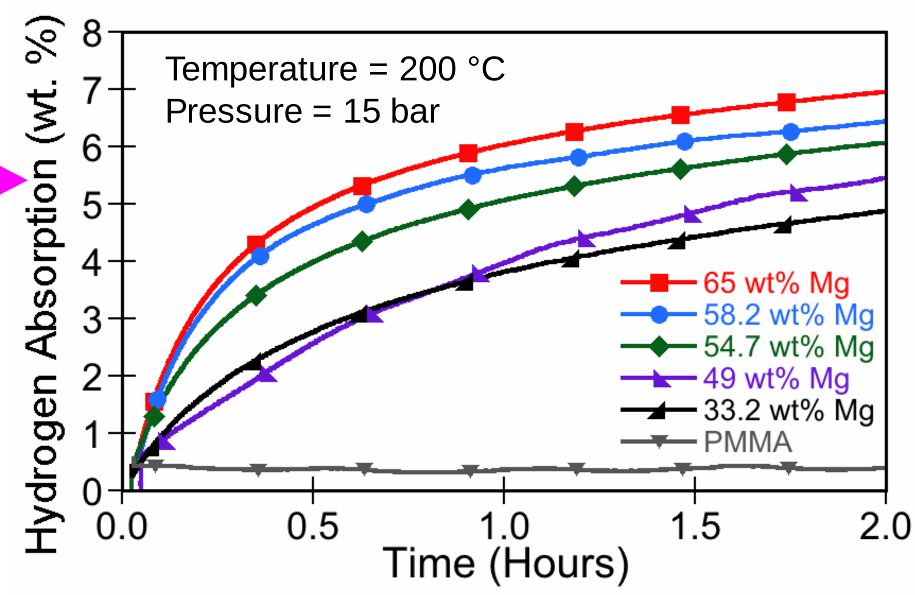
- Metal-hydride polymer nanocomposites can be a new platform for stable and high-performance gas storage

Nature Materials **2011**, 10, 286-290

BERKELEY LAB

Surprising Dual Enhancement of Storage and Stability



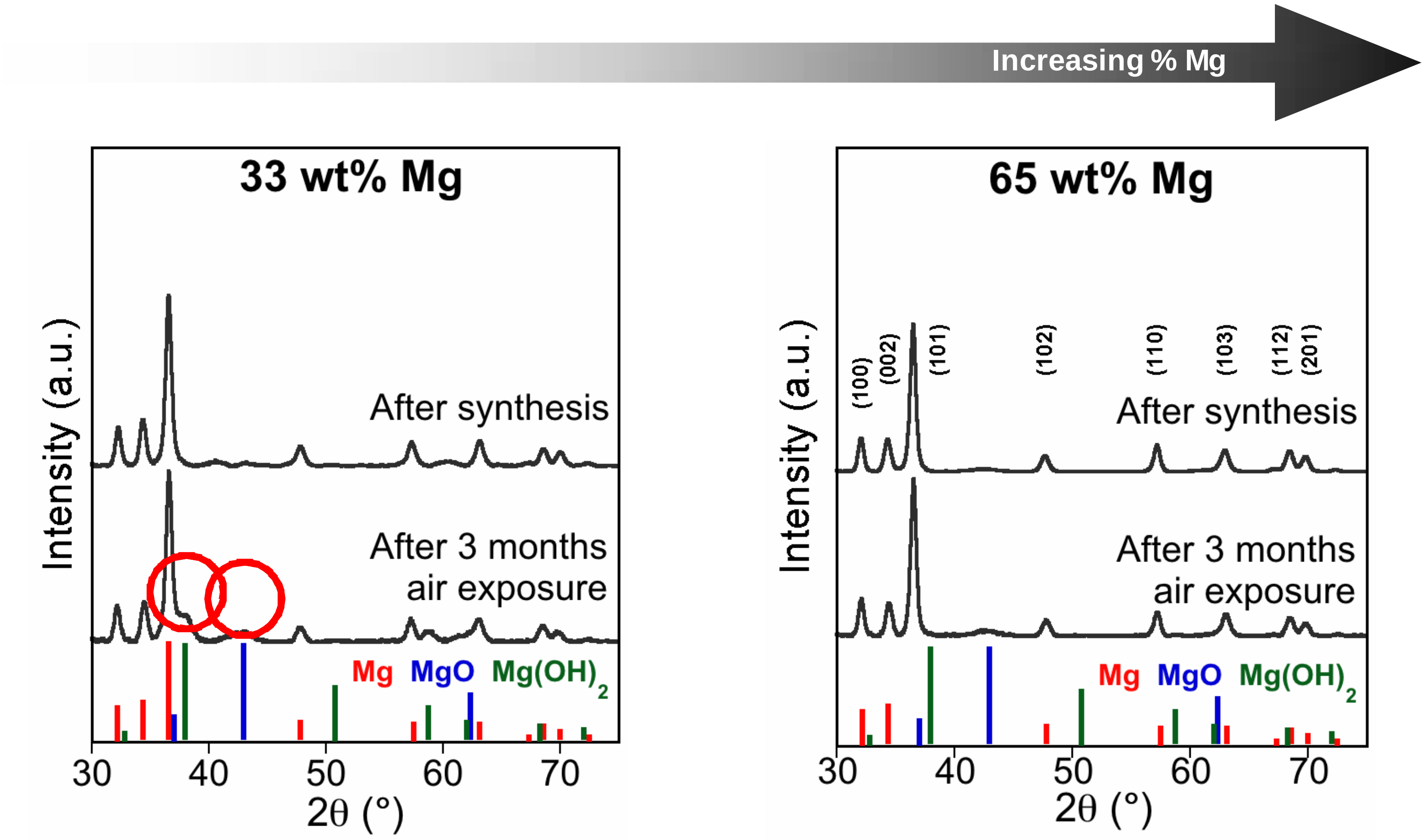


Remarkable dual enhancement drives up both loading and stability!

Now absorbing over 90% of theoretical maximum for Mg metal

Energy Environ. Sci., **2013**, 6, 3267–3271

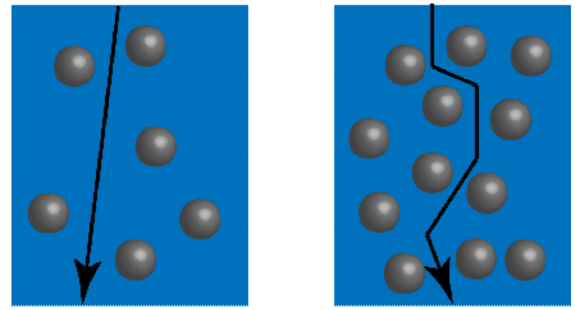
Counter-Intuitive Optimization: More Nanocrystals, Less Oxidation



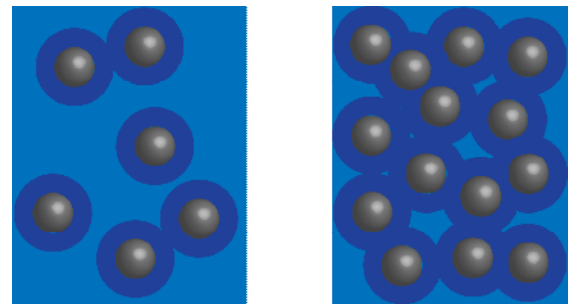
Energy Environ. Sci., **2013**, 6, 3267–3271

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

Factor [PMMA]	Wt% Mg	Vol% Mg	H_2 absorption, wt%
1.00	33.2 ± 0.9	25.4	4.86
0.75	49 ± 1	39.6	5.45
0.50	54.7 ± 0.6	45.2	6.07 vol% > 42
0.42	58.2 ± 0.6	48.8	6.44
0.30	65 ± 2	55.9	6.95

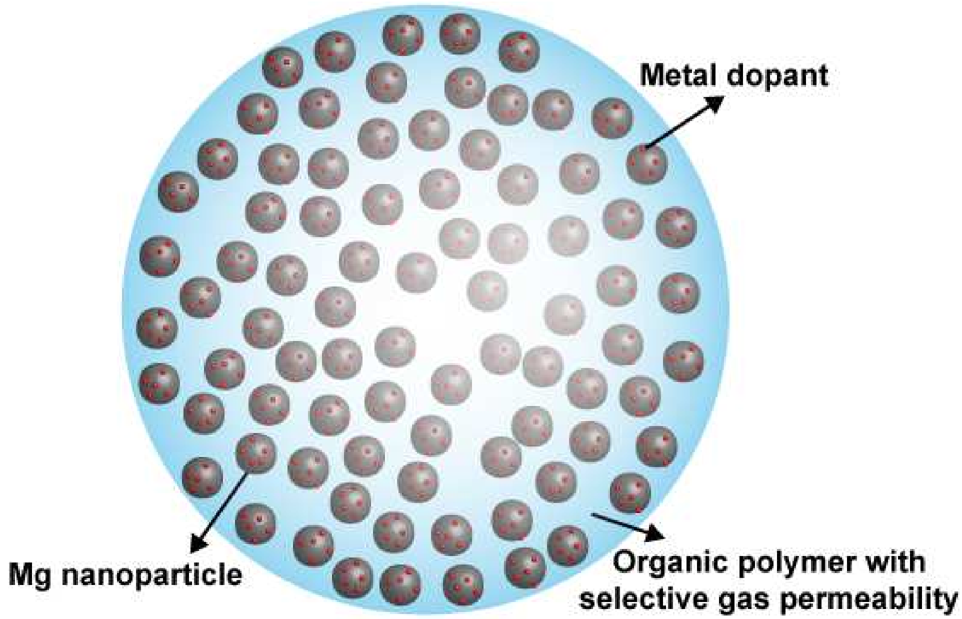
Molecular Foundry

J. Membr. Sci. **2006**, 270, 13-21
Phys. Rev. Lett. **2012**, 109, 118001

Enhancing the Kinetics of H_2 Sorption

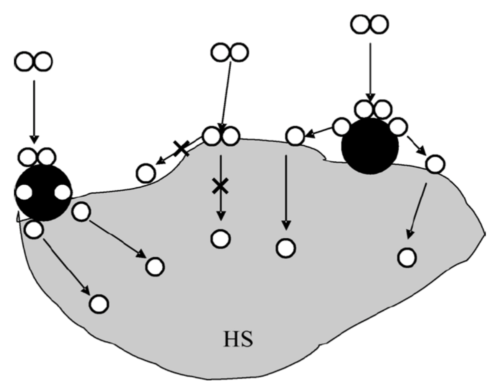
Capacity and stability are necessary, but not sufficient

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



Approach: Catalyst dopants

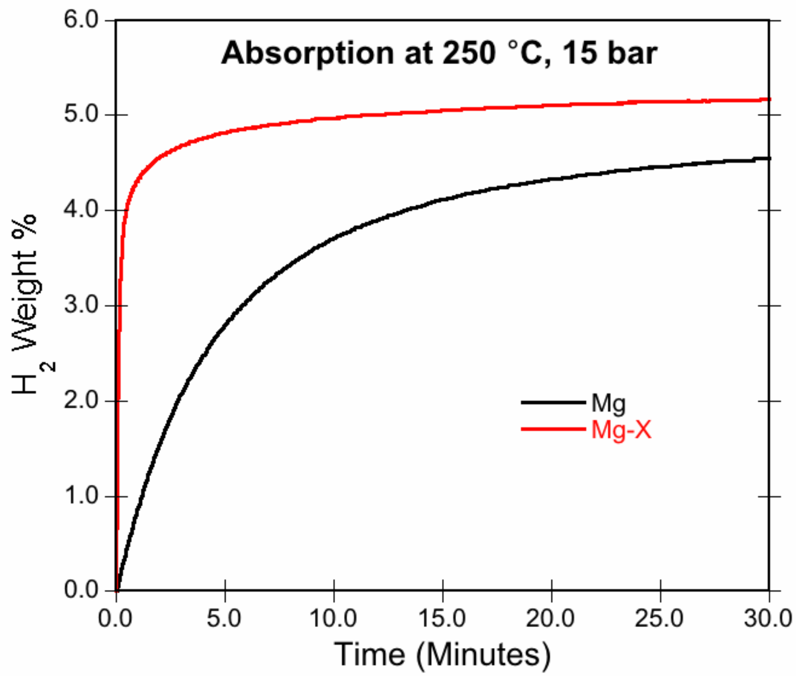
➔ Enhance dissociation of H_2 for better absorption, improved diffusion in hydrided phase

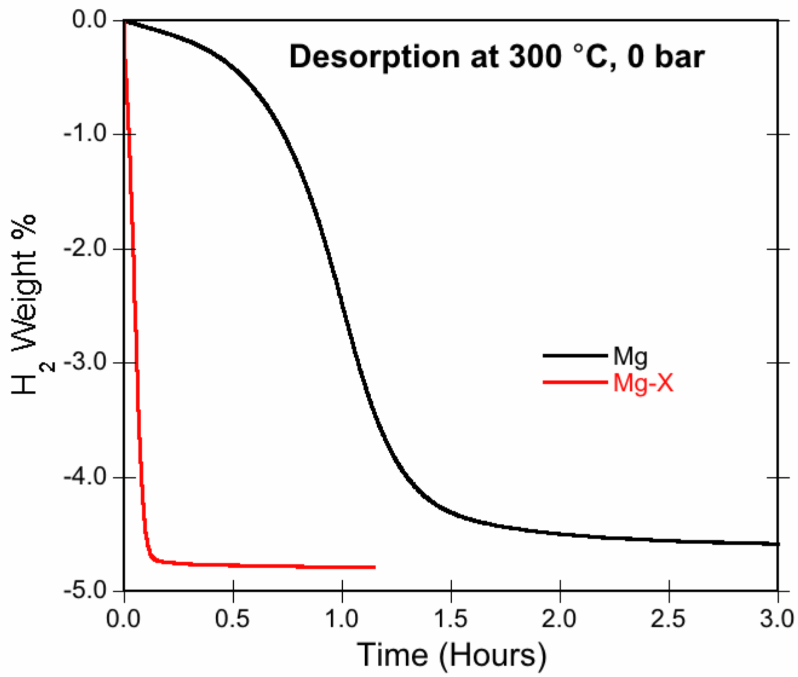


Molecular Foundry

BERKELEY LAB

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…

Molecular Foundry

Ruminski et al. *in preparation*

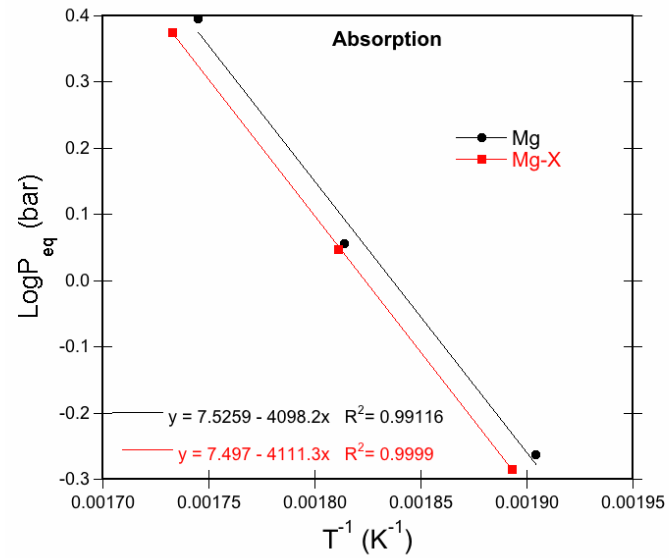
BERKELEY LAB

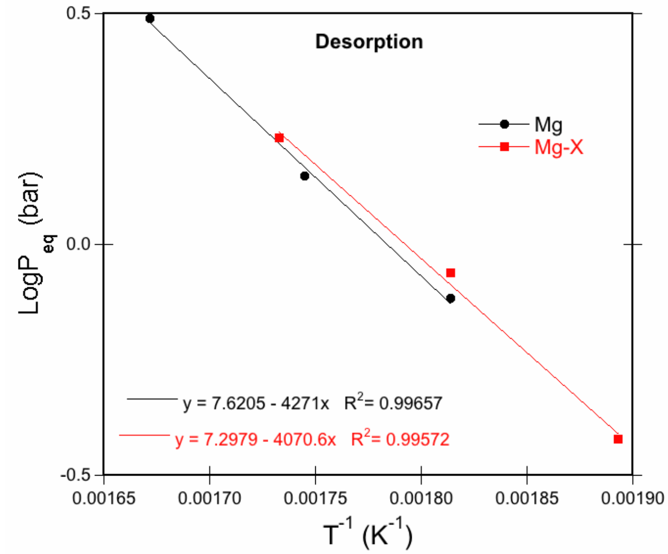
Mg Doping: Enhancing Kinetics of H2 Sorption

Absorption	ΔH (kJ/mol K)	ΔS (J/mol K)	Ea (kJ/mol)	P_{eq} @ 300 °C (bar)
Mg - bulk	-74.6	-135	95-130	
Mg	-34.1	-62.6	L 90.7 /P 99.7	2.5
Mg-X	-34.2	-62.3	L 69.5 /P 83.5	2.4

Shift in P_{eq} increases driving force

Desorption	ΔH (kJ/mol K)	ΔS (J/mol K)	Ea (kJ/mol)	P_{eq} @ 300 °C (bar)
Mg - bulk	75	130	120-160	
Mg	35.5	63.4	TBD	1.4
Mg-X	33.8	60.7	L 115.7/P 104.2	1.7





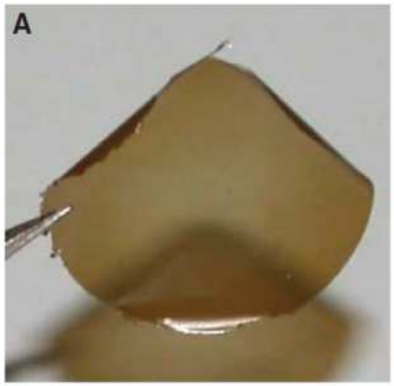
A.Ruminski et al. *in preparation*

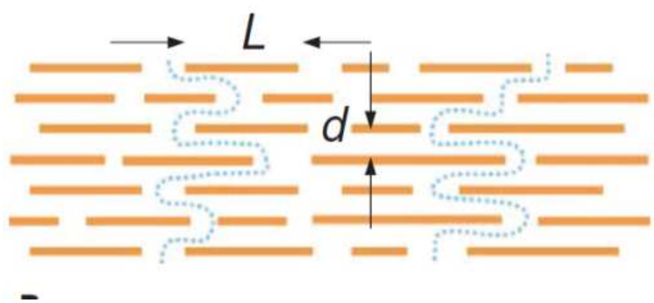
Molecular Foundry

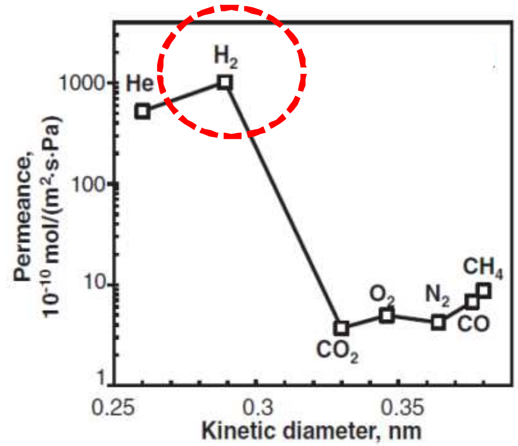
BERKELEY LAB

Toward the Atomic Limit for Separations: Graphene Layers as Gas Barrier

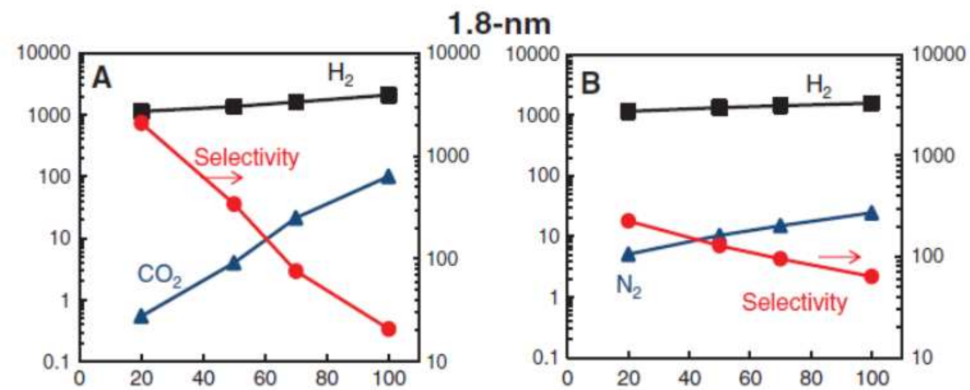
Graphene Oxide (GO) as a selective hydrogen barrier layer





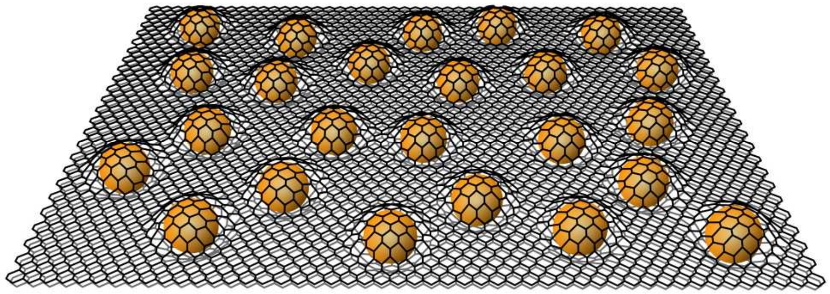


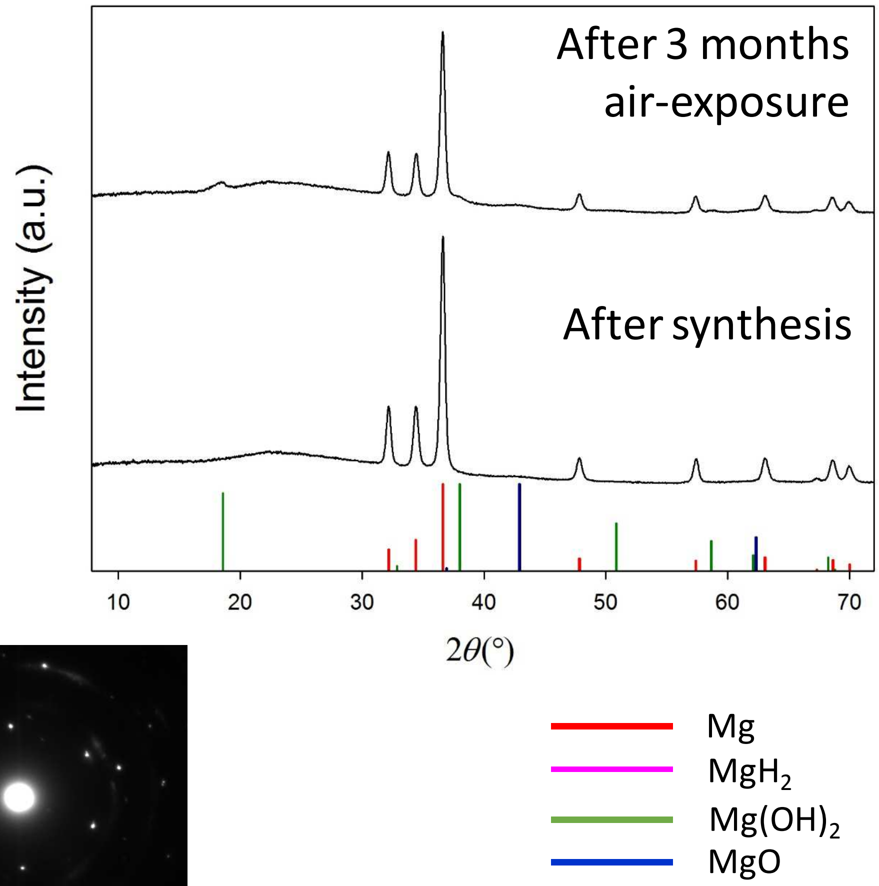
- GO layers exhibit high mixed gas separation selectivities: 3400 (for H_2/CO_2 mix) and 900 (for H_2/N_2 mixtures)

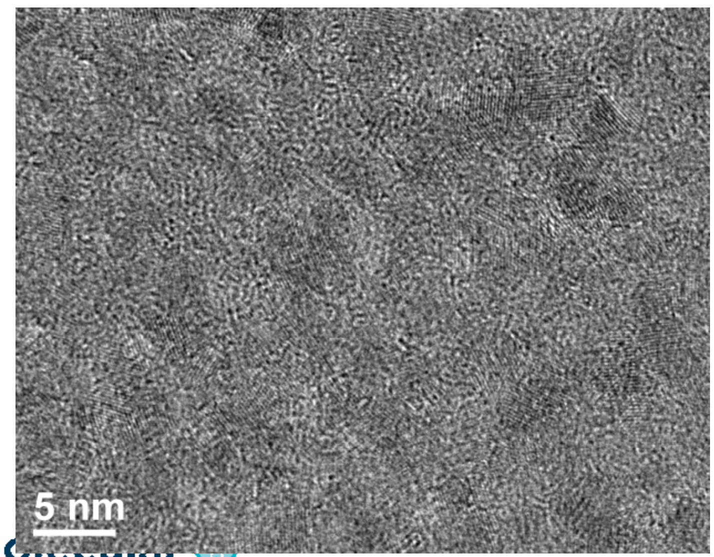


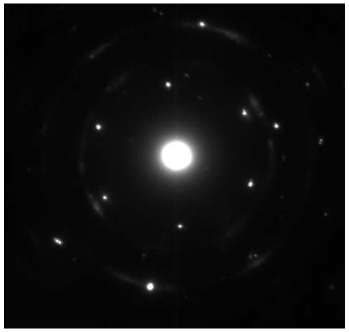
Science **2013**, 342, 95 *Science* **2013**, 342, 91 *Science* **2012**, 335, 441

Multilaminate “Ravioli” of Reduced Graphene Oxide (rGO) and Mg Nanocrystals



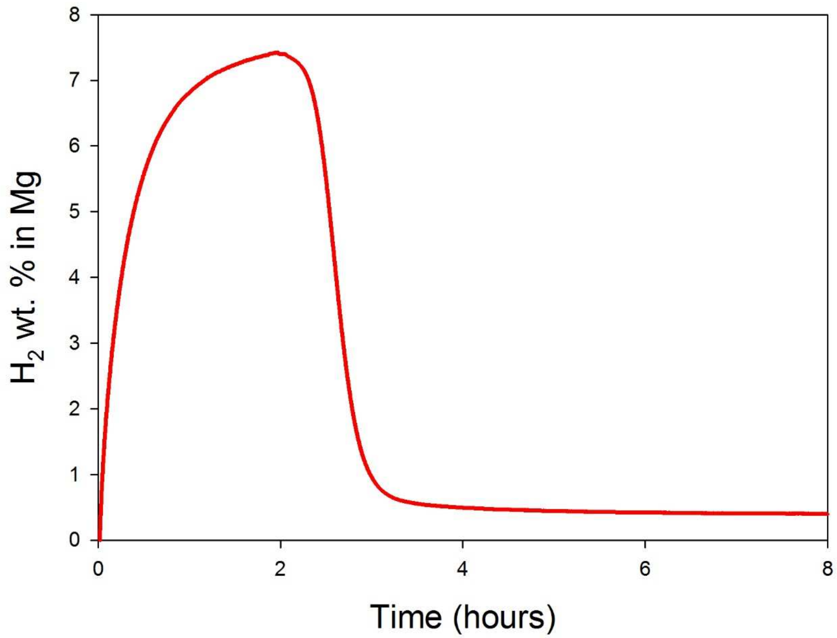


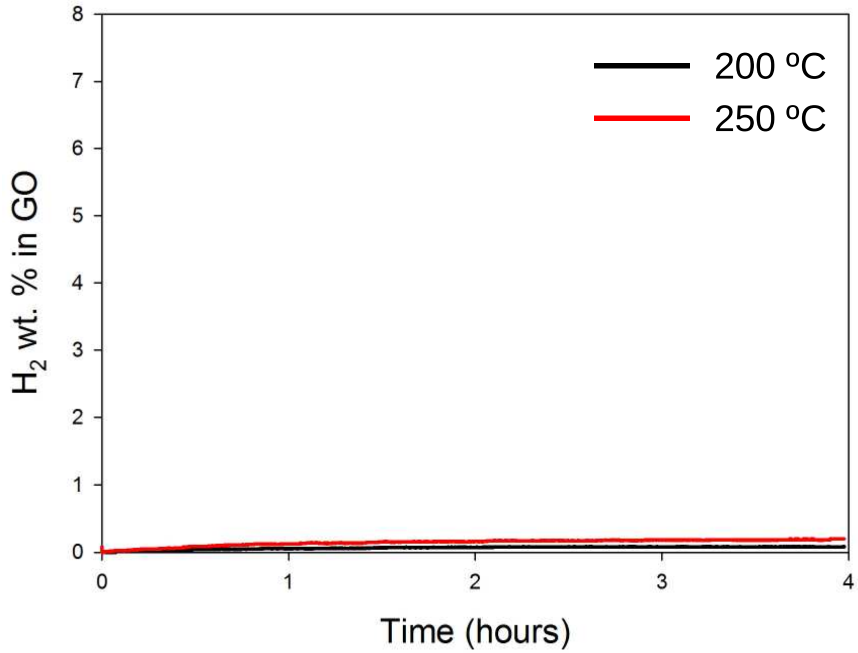




E.S.Cho et al, *submitted*

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%)
- H_2 sorption is 6.3 wt% for total composite (beyond FCEV target- 5.5%!)

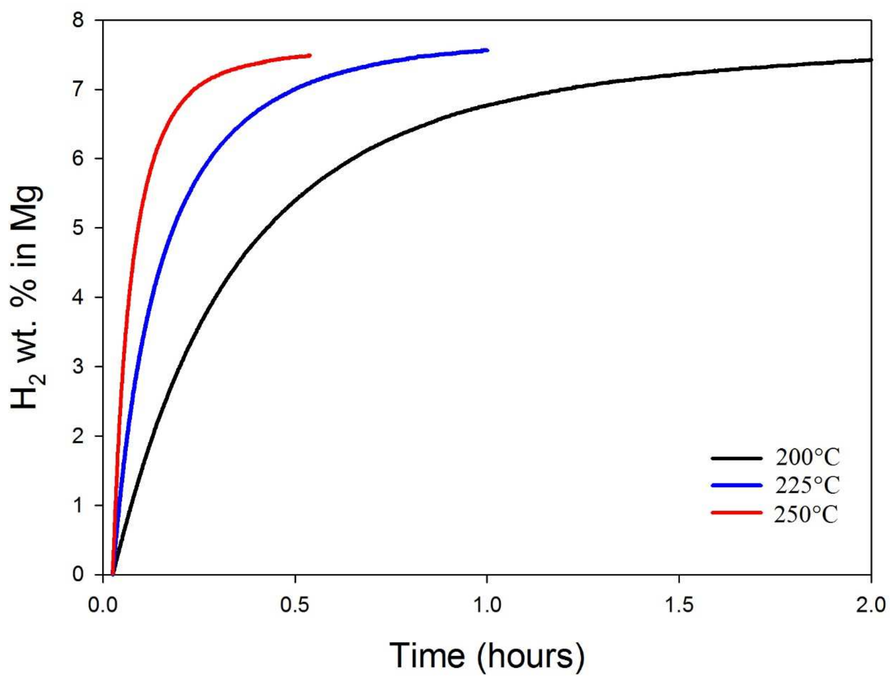
Molecular Foundry

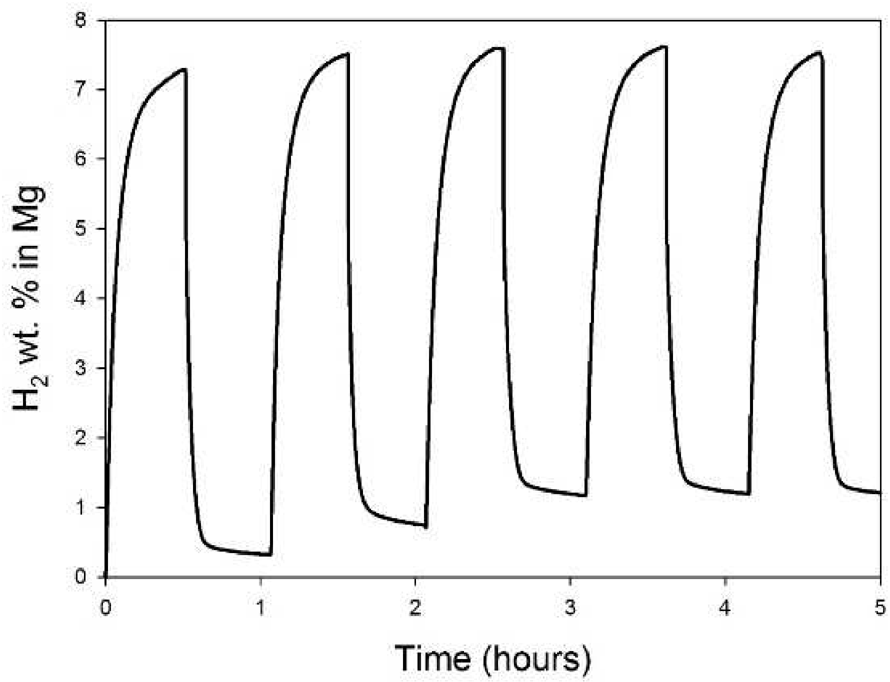
E.S.Cho et al, *submitted*

BERKELEY LAB

Cycling and Temperature Dependence

Cyclability and lower temperature performance are key metrics





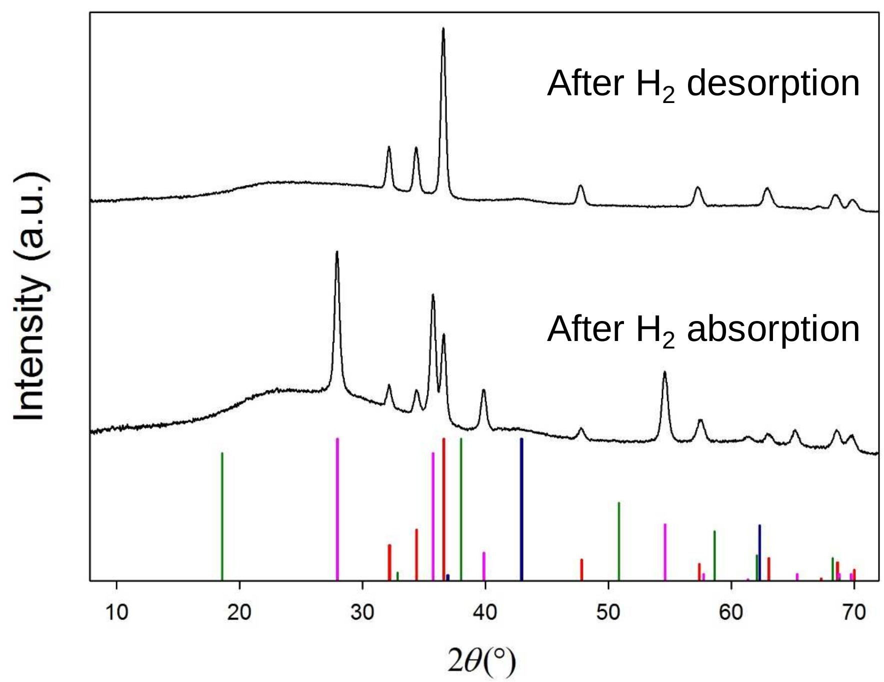
Multilaminate composite shows good cycle-ability and promise for low T

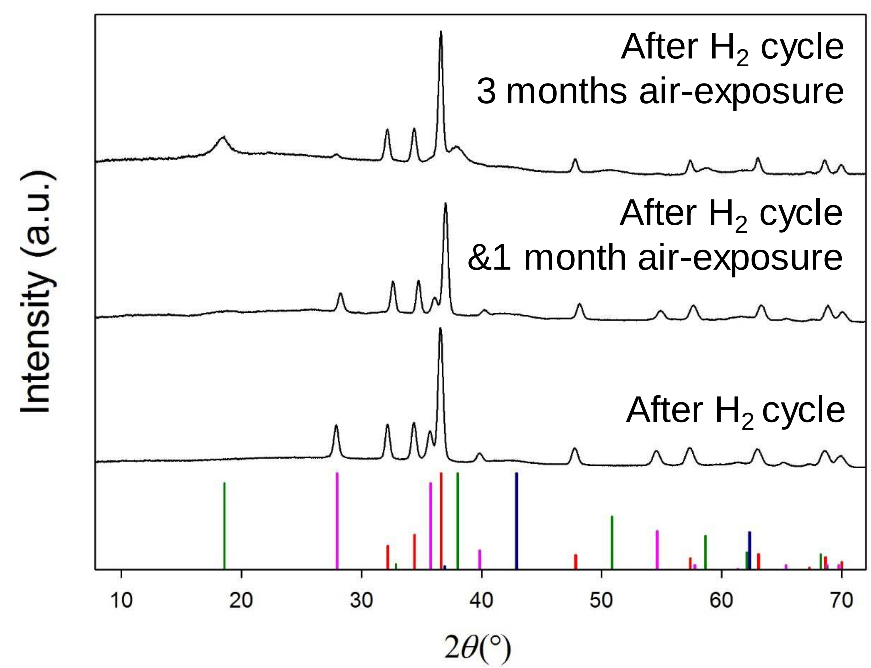
Molecular Foundry

E.S.Cho et al, *submitted*

BERKELEY LAB

Stability of Composite: Metallic Nano-Mg Air-Robust





Mg
MgH_2
$Mg(OH)_2$
MgO

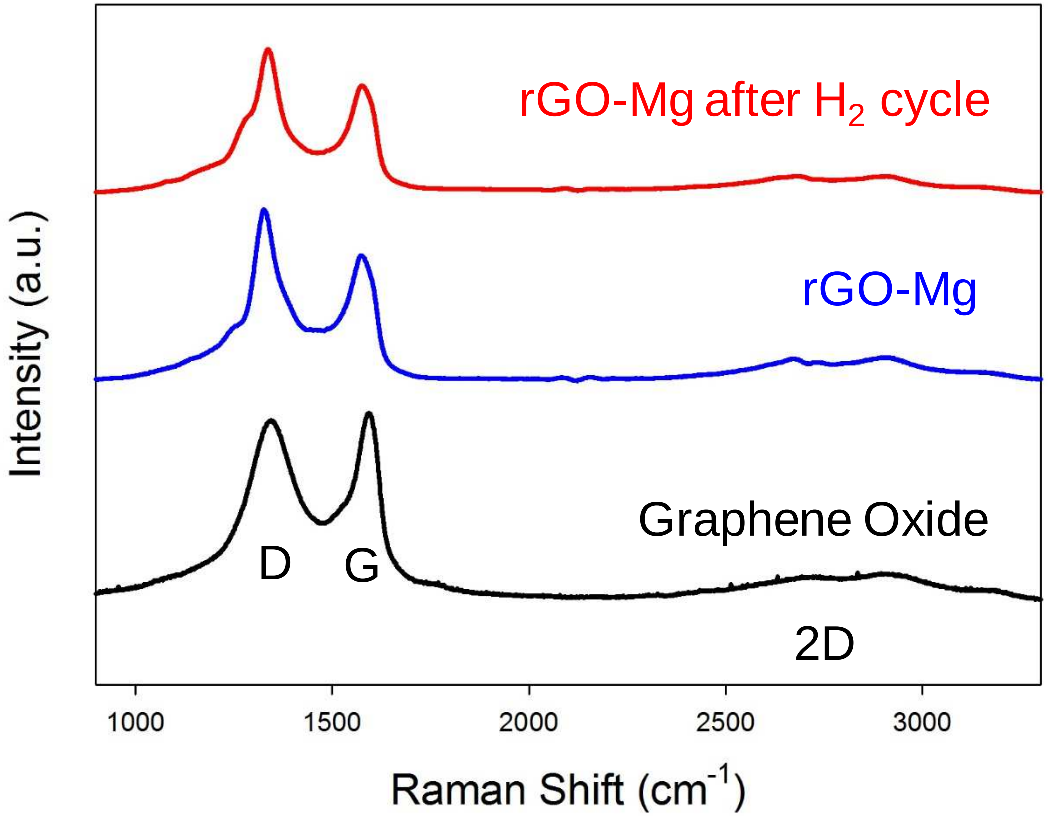
- The composite shows a combination of Mg and MgH_2 after cycling, and excellent air stability

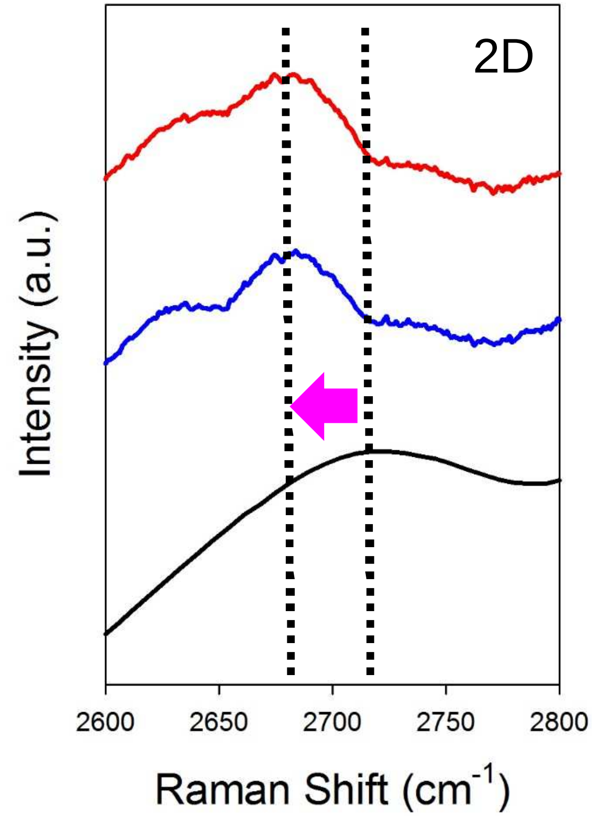
E.S.Cho et al, *submitted*

Molecular Foundry

BERKELEY LAB

Raman Spectroscopy on rGO-Mg Laminates

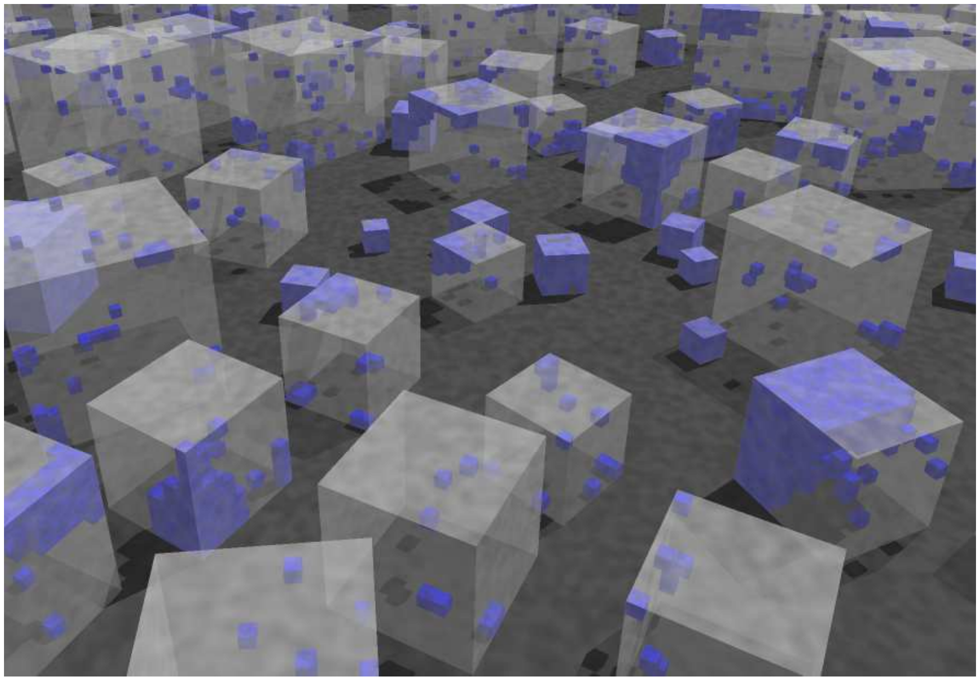


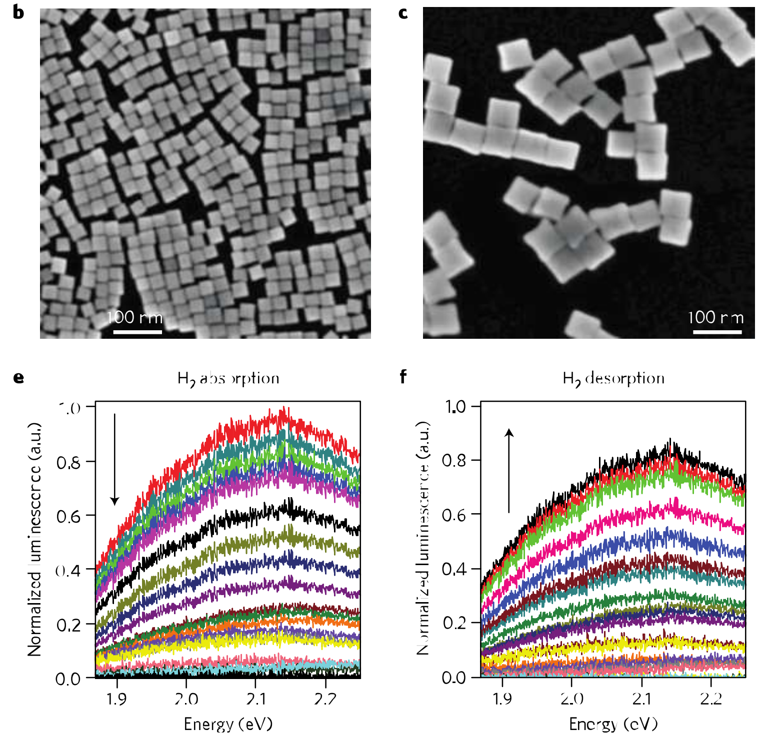


- D peak corresponds to defect sites and related to sp^2 domain size; the G peak originates from sp^2 C=C, and 2D peak provides information on the number of layers of graphene.
- I(D)/I(G) is increased after synthesis, consistent with GO reduction

E.S.Cho et al, *submitted*

In-Situ Methodology for Nanoscale Phase Transitions





Bardhan, Hedges, Whitelam, Urban *Nature Materials* (2013)

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

Molecular Foundry

BERKELEY LAB

Acknowledgements (This Work)

Staff Scientists/Engingeers (PIs)

Shaul Aloni

Peter Ercius

Post Docs/Students:

Anne Ruminski

Eun Seon Cho

Alyssa Brand

Funding support:

DOE – BES

BAPVC

SERIIUS

Proposal Call: Oct 1, 2014

Visit foundry.lbl.gov

Molecular Foundry

SERIIUS Solar Energy Research Institute for India and the United States

BAPVC BAY AREA PHOTOVOLTAIC CONSORTIUM

BERKELEY LAB