

IV.C.4 HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials

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Overall Objectives

- Focus on light materials and synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements via encapsulation and confinement.
- Design interfaces with chemical specificity for thermodynamic and kinetic control of hydrogen storage and sorption and selective transport.
- Explore novel storage concepts and/or obtain a fundamental understanding of established processes via known or idealized systems and materials.
- Develop in situ and in operando soft X-ray characterization capabilities in combination with first-principles simulations to extract atomic and molecular details of functional materials and interfaces.

Fiscal Year (FY) 2016 Objectives

- Develop graphene-encapsulated, metal-nanocrystal composites to produce environmentally-stable, high performance hydrogen storage materials.
- Optimize each material building block in the composite to derive the best performance possible by finely tuning the structure of encapsulating layers (graphene derivatives) and tailoring the elements and size of metal nanocrystals.

- Conduct X-ray spectroscopy characterization of model systems for solid-state metal hydrides.
- Produce mesostructured cellular foam (MCF)-17 with varying amounts of grafted Al, and assess population of acid sites, generate hydrogen adsorption isotherms, and study the impact of mesopore size and shape.
- Develop a predictive approach to simulate the X-ray absorption spectra of hydrogen storage materials under working conditions and begin studies of interfacial systems related to encapsulation of hydrogen storage media.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (A) System Weight and Volume
- (E) Charge/Discharge Rate

Technical Targets

This project will develop foundational understanding and new capabilities that will enable accelerated discovery of breakthrough materials in all classes of storage materials, in particular metal hydrides and sorbents. It is anticipated that the insights gained from this research, coupled with new synthetic, characterization, modeling, and database tools that will be made available to the hydrogen storage research community, will lead to materials that meet DOE targets such as system gravimetric and volumetric capacity, system fill time, and delivery temperature.

FY 2016 Accomplishments

- Designed a graphene encapsulation for metal nanocrystals with a solution-based synthetic approach. This is based upon prior work in the Urban group integrating polymers with metal hydrides, but represents a big step forward in using functional materials.
- Prepared 3 nm-sized Mg nanocrystals encapsulated by reduced graphene oxide (rGO) layers and achieved 6.5 wt% hydrogen capacity in terms of the total material weight with an excellent cyclability (detail in Figure 1).

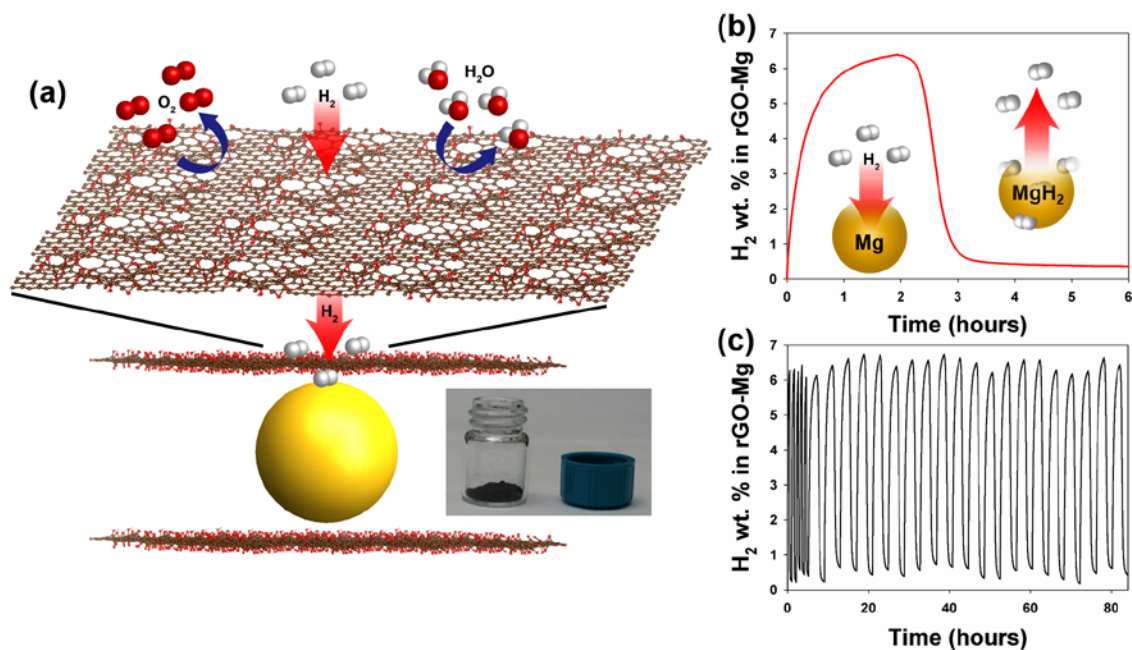


FIGURE 1. (a) Illustrations depicting the structure of the rGO-Mg composites where rGO layers prevent O_2 and H_2O from penetrating, while allowing the diffusion of H_2 (photograph of rGO-Mg in air). (b) Hydrogen absorption/desorption (at $200^\circ C$ and 15 bar H_2 / $300^\circ C$ and 0 bar) for the prepared rGO-M. (c) Hydrogen absorption/desorption cycling of rGO-Mg that were first exposed to air overnight. The first five cycles were performed at $250^\circ C$ and 15 bar H_2 / $350^\circ C$ and 0 bar, and the additional 20 cycles at $200^\circ C$ and 15 bar H_2 / $300^\circ C$ and 0 bar. As mentioned in the report we aim to translate these controls and insights into more complex metal hydrides moving forward.

- Exploited different kinds of graphene nanoribbons (GNRs) to encapsulate Mg crystals, accomplishing 7.1 wt% hydrogen capacity based on the total composite. Investigated the effect of different edge-functional groups of GNRs on the hydrogen adsorption (some examples in Figure 2; key point is that functional group differences can be linked to large [>30 kJ/mol] changes in enthalpy and corresponding rate enhancements).
- Synthesized 3d-transition metal doped rGO-Mg composite to enhance the hydrogen sorption thermodynamics and kinetics of Mg and studied their influence on hydrogen storage property of the composite. Collaboration with Lawrence Livermore National Laboratory on atomistic modeling of the dopant distribution was essential.
- Characterized structure and function in a series of candidate samples using in situ X-ray spectroscopic methods at the Advanced Light Source (ALS): Al_2O_3 , $LiAlH_4$, $NaAlH_4$, and Ti-doped $NaAlH_4$, $NaOH$, $NaHCO_3$, $NaNH_2$, NaH , $NaBH_4$, $NaAlH_4$ and Ti doped $NaAlH_4$ as the model systems.
- Identified an initial set of representative metal organic framework (MOF) structures with open metal sites to be characterized by the project team to obtain reliable experimental data to validate the corresponding computational efforts.
- Successfully produced mesoporous silica doped with varying amounts of aluminum by grafting method, permitting control of the density of acid sites (of the Lewis and Brønsted types) per unit internal surface area, characterized using a developed in situ cell for temperature-dependent Fourier transform infrared spectroscopy based on pyridine adsorption. Hydrogen adsorption isotherms were measured at low partial pressure and low temperature (below 1 atm and 77 K), indicating that condensation of hydrogen is insensitive to the size and shape of mesopores in our silica samples.
- Established first-principles simulations of X-ray absorption near-edge structure spectra of various standard hydrogen storage materials for comparison with existing literature and in tandem with ongoing measurements at ALS by J. Guo (LBNL) and began to explore the details of electronic interactions between magnesium surfaces and reduced graphene oxide and their ability to modulate hydrogen adsorption rates.



Graphene Nanoribbon (GNR)

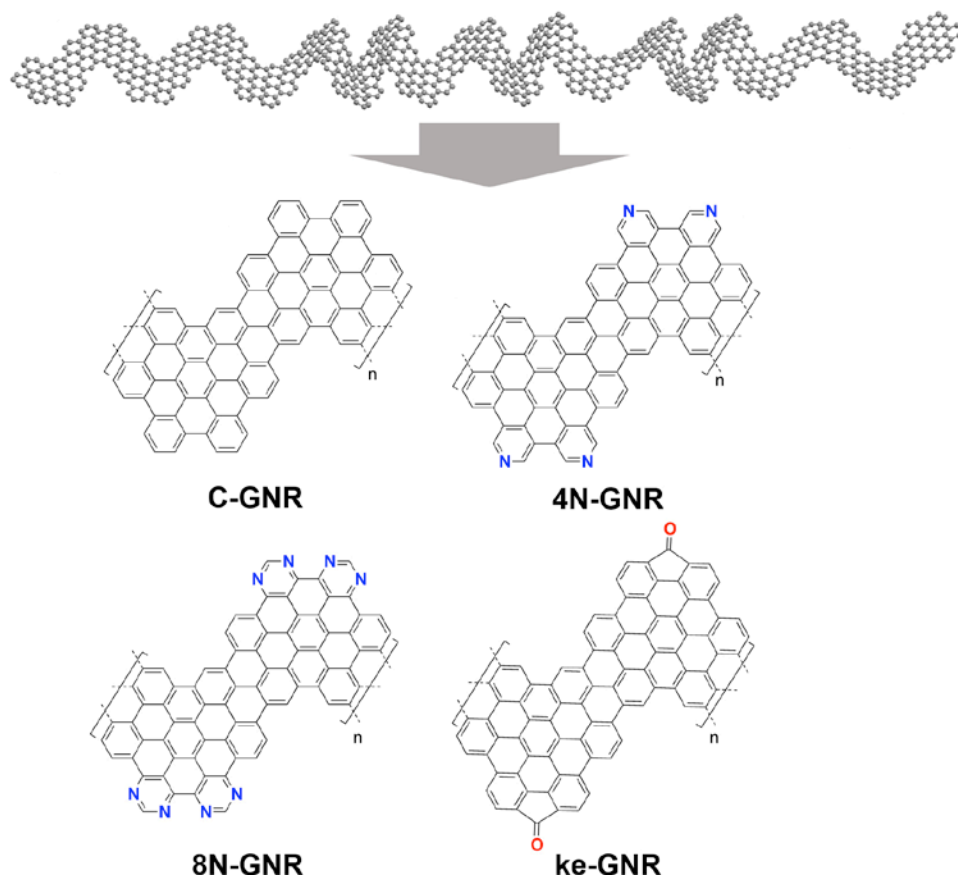


FIGURE 2. The chemical structures of GNRs with different edge-functional groups. As mentioned in the report, the intent is to use these chemical functionalities as a complementary extrinsic doping strategy to enhance the thermodynamics of metal hydrides.

INTRODUCTION

Storage of hydrogen onboard vehicles is one of the critical enabling technologies for creating hydrogen fueled transportation systems that can reduce oil dependency and mitigate the long-term effects of fossil fuels on climate change. Stakeholders in developing hydrogen infrastructure (e.g., state governments, automotive original equipment manufacturers, station providers, and industrial gas suppliers) are currently focused on high-pressure storage at 350 bar and 700 bar, in part because no viable solid-phase storage material has emerged. Nevertheless, solid-state materials, including novel sorbents and high-density hydrides, remain of interest because of their unique potential to meet all Fuel Cell Technologies Office targets and deliver hydrogen at lower pressures and higher onboard densities. A successful solution would significantly reduce costs and ensure the economic viability of a U.S. hydrogen infrastructure.

DOE-supported individual projects and the centers of excellence collectively synthesized and characterized hundreds of candidates documented in the DOE Hydrogen Storage Materials Database. Although materials meeting some of the key targets were identified, progress continues to be hindered by a lack of fundamental understanding of the kinetics and thermodynamics underlying the physical properties of interest. For sorbents, the biggest limitation is volumetric capacity within the target operating temperatures, whereas hydrides are limited by insufficient gravimetric capacity and/or reaction kinetics to meet the fill time target. At the recent Office of Energy Efficiency and Renewable Energy Material-Based Hydrogen Storage Summit, principal investigators prioritized the following major scientific challenges for the development of viable solid-state storage materials.

- Multi-scale model validation for developing metal hydride structure-property correlations.

- Computational tools to guide design of nanoporous sorbent pore size distributions.
- Synthetic strategies to increase the strength of H₂ interactions with sorbent adsorption sites.
- Rates and mechanisms of kinetic processes that limit metal hydride reversibility.
- Design rules for nanostructuring that improves metal hydride kinetics and thermodynamics.
- Models describing the structure, chemistry, and mass transport on surfaces and at interfaces.

APPROACH

The HyMARC consortium seeks to address these gaps by leveraging recent advances in predictive multiscale modeling, high-resolution in situ characterization, and material synthesis that were unavailable to the centers of excellence. Combined with materials informatics, this strategy embodies the approach highlighted within the recent Materials Genome Initiative Strategic Plan for accelerated materials development. By focusing on the underlying thermodynamic and kinetic limitations of storage materials, we will generate fundamental understanding that will accelerate the development of all types of advanced storage materials, including sorbents, metal hydrides, and liquid carriers. Thus, DOE investments will be fully leveraged for future external materials-focused projects. Clearly, Office of Energy Efficiency and Renewable Energy funding is essential, since the fundamental goals are too high risk for industry; such funding will allow establishment of the consortium as a Fuel Cell Technologies Office core capability.

Thermodynamics: Conceptually, the limitations of sorbents and hydrides can be thought of in terms of effective thermal energy required to release H₂, $\Delta E(T)$, and the corresponding gravimetric and volumetric capacities for a given material. $\Delta E(T)$ is comprised of thermodynamic and kinetic terms: $\Delta E(T) = \Delta H^\circ(T) + E_a$, in which $\Delta H^\circ(T)$ is the standard enthalpy of desorption at temperature T , and E_a is the activation energy for desorption. There are no materials today that meet the DOE requirements for $\Delta H^\circ(T)$ in large part because the targeted thermodynamics are in a mesoscale energy region where there are few examples, other than interstitial hydrides, which do not meet capacity targets. For sorbents, the targeted $\Delta H^\circ(T)$ (15–20 kJ/mol H₂) is stronger than van der Waals forces, but much weaker than covalent or ionic bonds. In contrast, $\Delta H^\circ(T)$ of high-capacity reversible metal hydrides is above the ≤ 27 kJ/mol H₂ target set by the engineering center of excellence. A major challenge, therefore, is to address the thermodynamic barriers to designing materials. The LBNL arm of the consortium is addressing this via new synthetic approaches to hybrid metal hydride sorbents, guided by theory and modeling, which

use an “inside-out” approach to doping: complementary internal additives (e.g., Ni, Co) with externally grafted graphene nanoribbons with targeted functional groups to lower transition state energies. Details of the atomic origins of these energetic changes and how to optimize these remain. Similarly, LBNL arm (Haranczyk) plans to use computational high-throughput screening to identify porous sorbents with strong H₂ binding sites such as MOFs with open metal sites. To enable such screening, an approach to introduce accurate description of hydrogen-binding site interaction needs to be implemented into molecular simulations of adsorption, an effort undertaken in collaboration with Lawrence Livermore National Laboratory team (Wood).

Kinetics: Kinetics also play a crucial role in determining H₂ uptake and release. Ideally E_a would be small for fast desorption and sorption; this is typically the case for sorbent materials, where $\Delta E(T) \approx \Delta H^\circ(T)$. However, E_a can be large (>50 kJ/mol) for many metal hydrides, causing materials that should be reversible thermodynamically to become unviable. The specific processes governing the slow kinetics may include bulk surface and interface mass transport processes, gas-surface reactions, and processes at solid-solid interfaces, including phase nucleation and growth. These phenomena are intrinsically interrelated, yet operate across broad ranges of length and time scales that make them difficult to characterize and model. Moreover, each is affected by chemistry, atomic structure, and microstructure in ways that are poorly understood. For example, certain additives can improve kinetics, but the lack of mechanistic understanding inhibits rational design. Dramatic improvements can also be obtained by reducing the critical hydride dimensions to the nanoscale. However, bulk approaches, such as ball milling, yield unacceptable heterogeneity in particle size, shape, and microstructure, whereas templating strategies using microporous hosts are unlikely to be practical due to the associated capacity loss. Properly leveraging these and other strategies for improving kinetics requires greatly increased fundamental understanding, but will require material platforms and characterization tools that enable individual processes and their interactions to be modeled and probed. Consequently, a second major challenge is to understand and prevent the kinetics of hydrogen desorption and uptake from making thermodynamically acceptable materials unusable. In addition to the work above, LBNL has established first-principles simulations of X-ray absorption near-edge structure spectra of various standard hydrogen storage materials for comparison with existing literature and in tandem with ongoing measurements at ALS and begun to explore the details of electronic interactions between magnesium surfaces and reduced graphene oxide and their ability to modulate hydrogen adsorption rates. This complements new in situ work being done on modified samples of this type.

Experimental Sample Handling: Our study showed that rGO-Mg composites have a self-protection layer which keep

the Mg nanoparticles (NPs) stable for a reasonable period of time. However, when performing experimental X-ray measurements at ALS for the NaAlH_4 and Ti-doped NaAlH_4 from Lawrence Livermore National Laboratory, sample preparation and transfer into the experimental system was critical. We have used glove box and vacuum suitcase to eliminate the possible exposure of the samples to air (water and O_2). The surface sensitive detection (total electron yield) and bulk sensitive detection (total fluorescence yield) were applied at the same time. Thus, the variation of surface and bulk chemical and structure properties can be utilized in the comparison with the first-principles simulations obtained by D. Prendergast [1]. Further in situ X-ray characterizations are carried out as the instrumentation is developed.

RESULTS

Theoretical Modeling of X-ray Spectroscopy Studies:

Using our previously developed first-principles approach to model X-ray absorption spectra (XAS) of materials (based on density functional theory [1]), we have explored a number of hydrogen storage materials to establish a predictive

capability for XAS simulation to provide interpretation of measurements to be made at ALS by J. Guo (LBNL) and others. In summary, we have found reasonable agreement at the sodium K-edge for a range of materials, including NaAlH_4 . We see less favorable agreement at the Al K-edge and we are currently exploring the reasons for this. We have had previous success in interpreting the spectra of molecular Al-organic crystals [2]. One possibility is that the very light H atoms require some accounting of their nuclear quantum distribution rather than a classical approximation that would afford them a much smaller spatial distribution about their average high symmetry positions at finite temperature. We see little effect on either absorption edge associated with Ti-dopants, as yet, apart from any phase separation into metallic (Al) or intermetallic (AlTi) phases, which clearly appear as intensity below the absorption edge of the hydrides.

We have also worked towards understanding the means by which selective and environmentally insensitive hydrogen adsorption occurs in Mg nanoparticles encapsulated in rGO, as demonstrated by Urban. We model the rGO in an initial ideal case as porous graphene (Figure 3a) and explore the pore size dependence of the activation energy for passage of

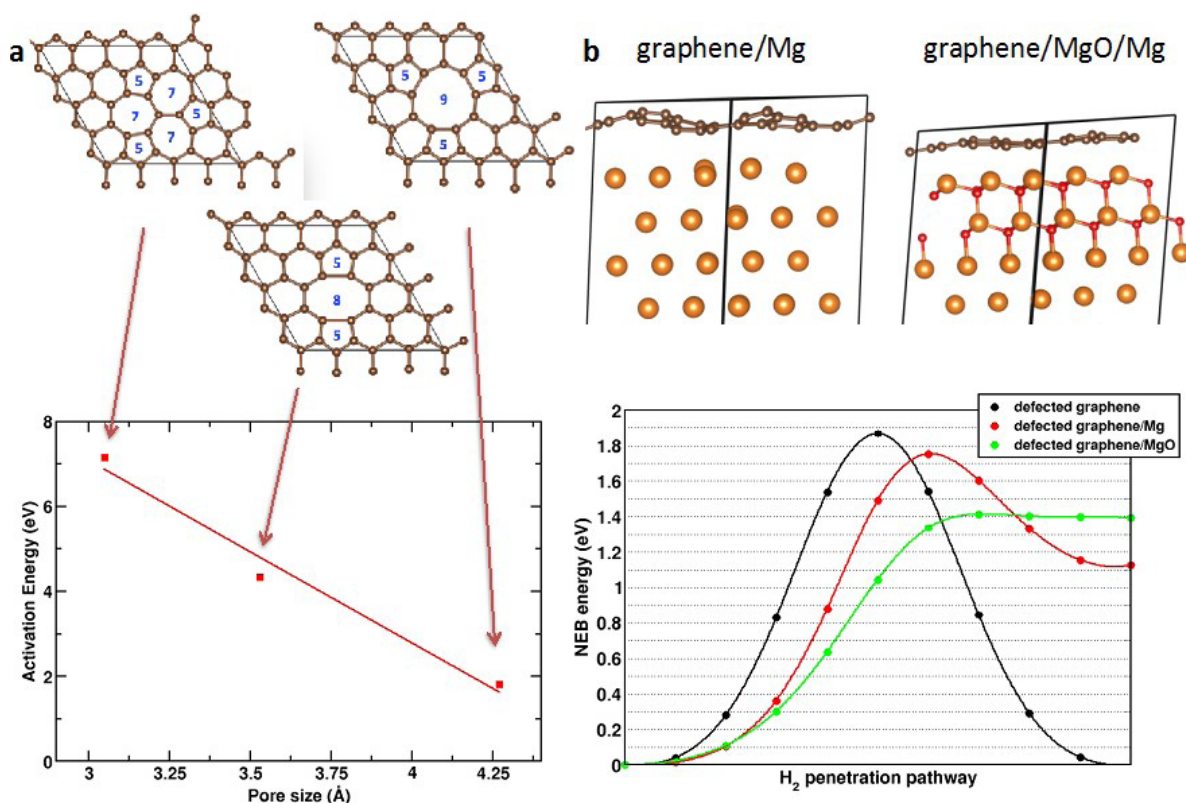


FIGURE 3. (a) Top: Various simple defects that result in pores in graphene: the 555-777 divacancy, the 5-8-5 divacancy, and the 555-9 tetravacancy. Bottom: The dependence of activation barrier in eV for dihydrogen to pass through various defects as a function of their pore size. (b) Top: The structure of 555-9 defective graphene on top of the (0001) surface of hexagonal close-packing Mg and a suboxide layer at the Mg surface. Bottom: Variation in the nudged-elastic-band energy profile (eV) for passage of dihydrogen through the 555-9 defect for just graphene (black), graphene on Mg (red), and graphene on an oxidized Mg surface (green).

a dihydrogen molecule across this atomically thin membrane. We find that the activation energy is inversely proportional to the minimum pore dimension (Figure 3b). In addition, for the largest pore dimension considered (the so-called Y-tetravacancy [3]) we note that contact with the [0001] Mg surface (for the bulk hexagonal close-packing phase) slightly reduces the activation barrier for the passage of dihydrogen through the pore. In addition, the presence of a few suboxide layers (introduced as interstitial defects in the Mg surface) greatly enhances the adhesion of graphene to the Mg surface and also further reduces the barrier to insertion of dihydrogen (Figure 3d). We will seek validation of this idealized picture through further XAS measurements to determine if any suboxide is present in the synthesized samples, possibly as part of the graphine oxide reduction process.

We have developed and synthesized a series of lightweight nanostructured materials derived from graphene and evaluated these structures as a stabilizing matrix for highly reactive (pyrophoric) metal (Mg, Al) nanoparticles used in hydrogen storage. The role of these atomically defined GNRs (Figure 2) in composite materials for hydrogen storage extends beyond a common support material but integrates the ability to rationally tune performance parameters such as selective gas permeability, high thermal conductivity, and the potential to incorporate molecularly defined catalysts that can promote the dissociation and association of dihydrogen during the loading and unloading processes. Our results show that Mg NPs embedded in a GNR matrix (<5 wt%) are stable to moisture and air (unprotected bare Mg NPs are pyrophoric) while fully retaining the high storage capacity inherent to the Mg/MgH₂ system. We further demonstrated that the selective introduction of functional groups along the edges of GNRs directly affects the adsorption and desorption kinetics. This experimental result supports a mechanism in which the immediate chemical environment created by

the functionalized GNRs stabilizes the rate determining transition state in the hydrogen uptake in Mg nanoparticles. Furthermore, we have embarked on the design and synthesis of GNRs featuring multidentate ligands for molecular-defined catalysts that promote the dissociation of dihydrogen in the immediate proximity of the metal NPs.

Spectroscopy and Characterization: Ti doped NaAlH₄ samples synthesized by V. Stavila (Sandia National Laboratories) were found to have dramatic changes in kinetics even with very low doping concentration. The experimental XAS characterization on Al and Na K-edge was performed at ALS. The results have been analyzed and compared with theoretical simulation as described above. The effect of Ti doping is also investigated by the Ti L-edge XAS shown in Figure 4. The precursor TiCl₃ used in the synthesis is displayed as the reference comparison. The XAS spectral shape of the hydrogenated and dehydrogenated forms of 10 mol% Ti doped NaAlH₄ sample suggests an amorphous phase around the Ti local structure, which is in line with the expectation of V. Stavila. However, the neighboring coordination of Ti remains further study. Also the 10 mol% Ti doped NaAlH₄ sample shows a small portion of TiCl₃ preserved in the dehydrogenated form.

Sorbents (Theory): Our goal for the first year was to establish necessary references and benchmarks for the development of ab initio H₂ adsorption isotherm calculations for MOFs with open metal sites. This effort included selection of representative MOFs with open metal sites, and gathering reliable experimental data as well as a set of verified and curated crystal structures necessary to conduct simulations. The resulting material set includes CuBTC, PCN-14, NOTT-100–NOTT-103 series, and the MOF-74 analogue series with various metal types. Furthermore, we conducted a literature search to identify available models and classical potentials for prediction of H₂ adsorption within MOFs, and set up a

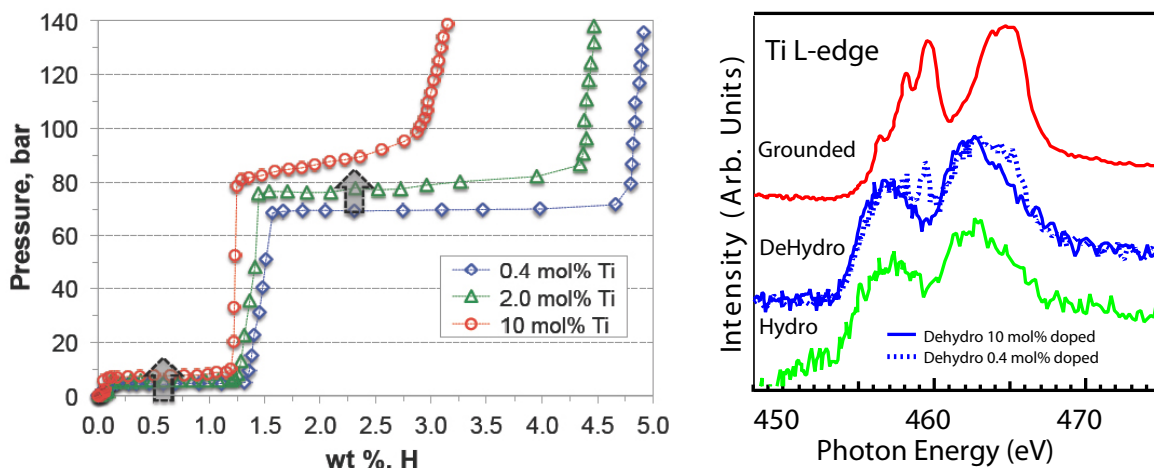


FIGURE 4. (Left) Increasing the concentration of TiCl₃ in NaAlH₄ leads to increased plateau pressures. (Right) X-ray absorption spectroscopy spectra of TiCl₃ grounded mixing and Ti doped NaAlH₄.

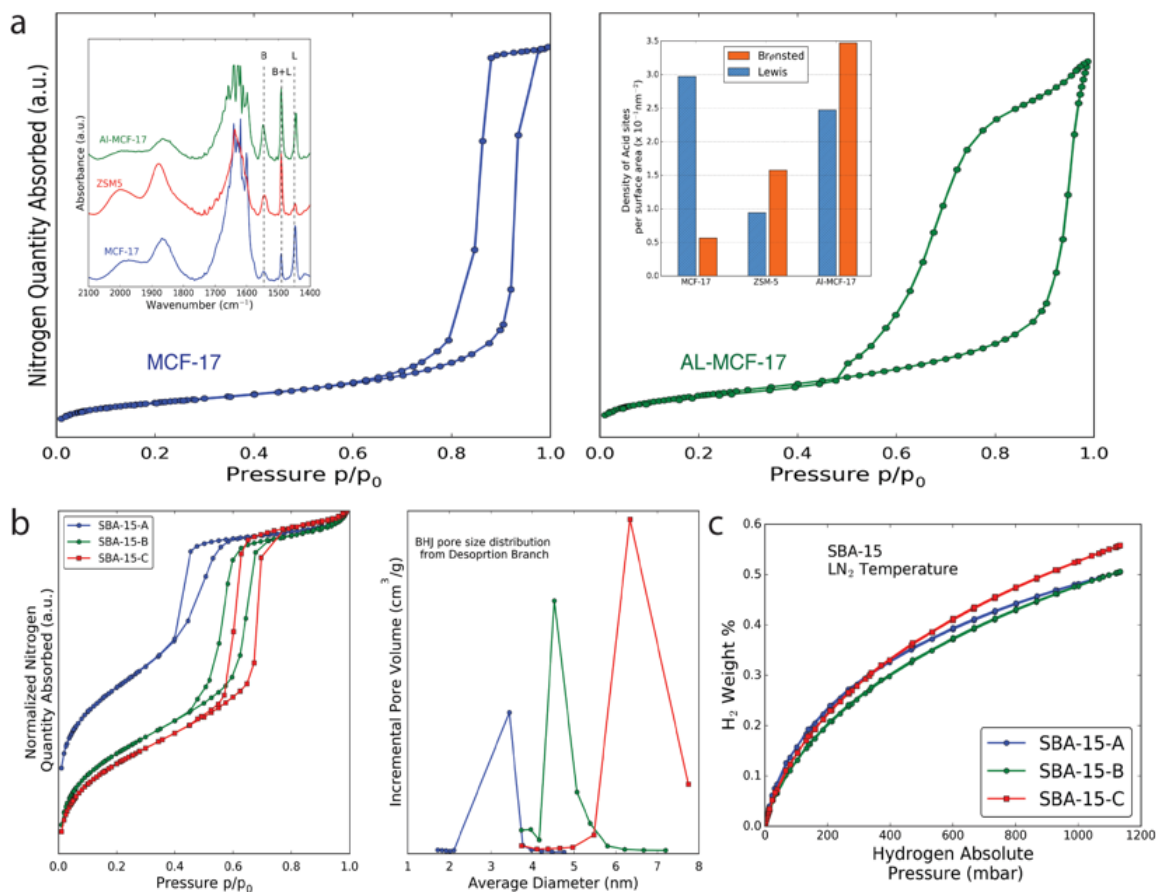
grand-canonical Monte Carlo simulation code, RASPA, to execute those. We also investigated available approaches to include polarizable electrostatic interactions between the H_2 quadrupole moment and MOF atoms. For each MOF in our experimental test set, we obtained H_2 adsorption isotherms at 77 K and 298 K using the available approaches, and identified errors with respect to experimental results. This effort has set benchmarks for the following effort to introduce ab initio isotherm calculations for the selected systems.

Sorbents (Experiment): We developed a technique to dope silica with aluminum as a means to introduce acid sites (Lewis and Brønsted acids) in mesoporous structures. We were able to dose these sites using infrared spectroscopy and pyridine adsorption (Figure 5, Table 1, Table 2). These samples are currently under investigation to determine if the

acid sites influence the hydrogen adsorption properties (wt% adsorbed, kinetics, and thermodynamics).

CONCLUSIONS AND FUTURE DIRECTIONS

Theory of X-ray spectroscopy: Thus far in our simulation efforts, we have shown that we can accurately predict Na K-edge X-ray absorption near-edge spectroscopy but that we have some issues in predicting those at the Al K-edge. We will explore issues related to sample handling, self-absorption in the X-ray absorption near-edge spectroscopy measurement and fundamental issues related to the broader quantum nuclear distribution of hydrogen atoms in hydrides, which to date have been approximated at classical particles. We also see a strong dependence on pore size and interfacial



a.u. – Arbitrary units

FIGURE 5. (a) Nitrogen adsorption isotherms for, (left) MCF-17 and (right) Al-MCF-17. For both measurements, the nitrogen adsorption was done at liquid nitrogen temperature prior to which water was evacuated by degassing the samples at 450°C under vacuum. (left) Evaluation of MCF-17 and Al-MCF-17 acid sites using pyridine adsorption and infrared spectroscopy (transmission mode). (right) Density of sites per surface area of samples. (b) Physisorption experiments on Santa Barbara Amorphous (SBA)-15: (left) normalized nitrogen adsorption isotherms for sample A, B, and C; (right) the pore size distribution according to the Barrett-Joyner-Halenda model in terms of incremental pore volume. Measurements at liquid nitrogen temperature after the samples have been degassed at 450°C under vacuum for 5 h (remove water). (c) Hydrogen adsorption isotherms on the SBA-15 samples. Experiments were run at liquid nitrogen temperature and samples were degassed at 450°C under vacuum prior to testing.

The surface area was extrapolated using the Brunauer-Emmett-Teller (BET) theory model. The average mesoporous diameter and volume were obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda model. The micropores volume was derived from the isotherms using the t-plot methodology (Table 1, Figure 5).

TABLE 1. Summary of the Data Obtained by Nitrogen Physisorption Measurements (see Figure 5)

Samples	Surface Area (m ² /g)	Average Porous Diameter (nm)	Mesopores Volume (cm ³ /g)	Micropores Volume (cm ³ /g)
MCF-17	672	23.6	3.18	0.0016
Al-MCF-17	473	25.0	1.71	0.0010

The surface area was extrapolated using the BET model. The average mesoporous diameter and volume were obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda model. The micropores volume was derived from the isotherms using the t-plot methodology (Table 2, Figure 5).

TABLE 2. Summary of the Data Obtained by Nitrogen Physisorption Measurements (see Figure 5).

Samples	BET (m ² /g)	Average Porous Diameter (nm)	Mesopores Volume (cm ³ /g)	Micropores Volume (cm ³ /g)
SBA-15-A	525	3.3	0.25	0.091
SBA-15-B	760	5.0	0.55	0.093
SBA-15-C	810	6.2	0.65	0.099

interactions in the activation energy for the passage of dihydrogen molecules through defective graphene, which we propose as a model for the rGO encapsulated magnesium nanoparticles. We will continue to add more realistic detail to this model of the system synthesized by Urban and try to explain the success of this nanoscale composite in terms of chemical stability to atmospheric impurities, such as oxygen, water, and carbon dioxide. We will also pursue validation of this model through X-ray based characterization at ALS.

Spectroscopy at ALS: The experimental characterization at ALS will continue on the modeled systems. We learned from our measurement that the existing literature does not have a reliable XAS spectrum even for the standard NaAlH₄. Thus, we need to perform the study of aging effect for the sensitive samples, and possibly synthesize new samples using different precursors and/or different protocols.

Mg Nanocrystals Encapsulated by Graphene Derivatives at Urban Group: The Urban group has synthesized Mg nanocrystals wrapped by different kinds of graphene derivatives, including graphene oxide layers. Transition metal dopants, particularly Ni, have been added to this system for the purpose of improving hydrogen sorption kinetics. In our material system, both high capacity and kinetics have been achieved, along with good air stability and cyclability. We learned that doping on metal hydrides can be managed with different material elements which ultimately tweak the hydrogen sorption properties of the composite material. In the future study, we will pursue the graphene

wrapping system with different kinds of metal and complex hydride materials such as Mg(BH₄)₂; and, different kinds of doping will be attempted to optimize the hydrogen sorption properties of the materials

We intend to expand the scope of GNR composite nanomaterials by developing structures that are competent at stabilizing Al NPs featuring a higher theoretical hydrogen storage capacity. We will further explore the unusual mechanism by which GNR supports modulate the H₂ absorption and desorption kinetics and the surface of Mg NPs. This very fundamental exploration will heavily rely on new characterization tools developed through HyMARC such as a hydrogen gas flow cell compatible with in situ X-ray spectroscopy.

Sorbents: Measurement of adsorption isotherms at pressures up to 100 bar on inorganic samples are complex, and we are currently developing a method, in collaboration with Quantachrome, to succeed in this field. Our plan for the next fiscal year is to acquire a high pressure system allowing for testing of our sample under high pressure and various temperature (from cryogenic to room temperature) to obtain thermodynamics and kinetics information. We plan on investigating the structural effect of inorganic support such as the meso- and micropores at high pressure. In parallel, acid samples and metal loaded samples will be investigated to figure if these additives can serve as catalytic add-ons to improve molecular hydrogen adsorption.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Jeffrey J. Urban, Eun Seon Cho, Anne M. Ruminski, Shaul Aloni, Yi-Sheng Liu, Jinghua Guo, “Graphene Oxide/Metal Nanocrystal Laminates: the Atomic Limit for Safe, Selective Gas Storage,” US patent application serial no. 62/203, 198, filed on August 10, 2015.
2. Felix R. Fischer, Jeffrey J. Urban, Eun Seon Cho, Anne M. Ruminski, Ryan Cloke, Tomas Marangoni, Cameron Rogers, “Nanostructured Composites for Gas Separations and Storage,” US patent application serial no. 62/157, 952, filed on May 6, 2015

FY 2016 PUBLICATIONS/PRESENTATIONS

Publications

1. Eun Seon Cho, Anne M. Ruminski, Shaul Aloni, Yi-Sheng Liu, Jinghua Guo, Jeffrey J. Urban, “Graphene Oxide/Metal Nanocrystal Multilaminates as the Atomic Limit for Safe and Selective Hydrogen Storage,” *Nature Communications*, 7 (2016), 10804.

Presentations

Jeffrey J. Urban

1. July 2016—Department of Chemical Engineering, EPFL Sion, Switzerland (Invited).
2. July 2016—Department of Materials Engineering, ETH Zurich, Switzerland (Invited).
3. May 2016—Presentation to International Panel of Hydrogen and Fuel Cells for the Economy, Berkeley, CA (Invited).
4. April 2016—Department of Chemical Engineering, Stanford University, Palo Alto, CA (Invited).
5. April 2016—Presentation to Technical Team of Hydrogen Fuel Cell Manufacturers, Berkeley, CA (Invited).
6. April 2016—Department of Applied Physics, Eindhoven University, Netherlands (Invited).

Felix R. Fischer

1. Department of Chemistry Seminar Swiss Federal Institute of Technology, Zurich, Switzerland, November 16, 2015.
2. Department of Chemistry Seminar Columbia University, New York, NY, U.S.A., January 28, 2016.
3. Department of Chemistry Seminar Boston College, Boston, MA, U.S.A., February 2, 2016.
4. Department of Chemistry Seminar Massachusetts Institute of Technology, Boston, U.S.A., February 3, 2016.
5. Department of Chemistry Seminar Stanford University, Stanford, CT, U.S.A., February 10, 2016.

6. Department of Chemistry Seminar Northwestern University, Evanston, IL, U.S.A., February 26, 2016.
7. Dozententagung, German Chemical Society, Heidelberg, Germany, March 21–23, 2016.
8. Department of Chemistry Seminar University of California San Diego, San Diego, CA U.S.A., April 11, 2016.
9. Department of Chemistry Seminar California Institute of Technology, Pasadena, CA, U.S.A., April 13, 2016.
10. Department of Chemistry Seminar Cornell University, Ithaca, NY, U.S.A., May 1, 2016.
11. Max-Planck Institute for Carbon Research, Muelheim, Germany, May 18, 2016.
12. Department of Chemistry Seminar Technical University of Dresden, Dresden, Germany, May 25, 2016.
13. Department of Chemistry Seminar Technical University of Braunschweig, Braunschweig, Germany, May 27, 2016.

Jinghua Guo

1. “In-Situ/Operando and High Pressure Soft X-Ray Spectroscopy of Chemical Reactions,” The 1st Workshop on Synchrotron Radiation Research and Energy Science between FUNSOM-ALS, Soochow University, Suzhou, China (October 28–29, 2015).
2. “In-Situ/Operando Soft X-Ray Spectroscopy of Catalytic and Electrochemical Reactions,” The 9th International Conference on Inelastic X-ray Scattering (IXS2015), NSRRC, Hsinchu, Taiwan (November 22–26, 2015).
3. “Probing the Optical Property and Electronic Structure of Nanostructured TiO₂,” MRS2016 Spring Meeting, Symposium EE14 - Titanium Oxides: From Fundamental Understanding to Applications, Phoenix, AZ (March 28–April 1, 2016).
4. “Insights of Catalytic and Electrochemical Reactions from the In-Situ/Operando Soft X-Ray Spectroscopy,” Department of Chemistry, Boston College, MA (April 4, 2016).
5. “Perspectives of In-Situ/Operando Soft X-Ray Spectroscopy in Energy Science,” X-Ray & Electron Spectroscopies, Uppsala, Sweden (15–17 June 2016).

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1. Prendergast, D.; Galli, G. “X-ray adsorption spectra of water from first principles calculations.” *Phys. Rev. Lett.* 96, 215502 (2006).
2. Altman, A. B. et al, “Theory and X-ray Absorption Spectroscopy for Aluminum Coordination Complexes – Al K-Edge Studies of Charge and Bonding in (BDI)Al, (BDI)AlR₂, and (BDI)AlX₂ Complexes.” *J. Am. Chem. Soc.* 137, 10304 (2015).
3. Robertson, A. W. et al, “Stability and Dynamics of the Tetravacancy in Graphene.” *Nano Lett.* 14, 1634 (2014).