
Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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Overall Objectives

- Develop a carbon-based, functionalized material prepared by new methods (graphene) or old (exfoliated graphite) with a capacity for hydrogen storage by physisorption of 11 wt% excess and 40 g/L total (near 77 K and <100 bar), a near-constant isosteric heat of adsorption, excellent kinetics, and long cycle life.
- Understand how far hydrogen physisorption capacity can be extended beyond the present rules of thumb for carbon materials (e.g., 1 wt% excess per every 500 m²/gram). The goal is achieving >1.5 wt% excess per every 500 m²/gram.
- Demonstrate a near-constant isosteric heat of adsorption, excellent kinetics, and long cycle life.

Fiscal Year (FY) 2018 Objectives

- Identify the role of low dimensional structure and validate >40 g/L total adsorption using multi-temperature analysis over 77 to 160 K for isosteric heat validation >10 kJ/mole.

- Achieve ≥ 1.5 wt% excess hydrogen per 500 m²/g in material with >3,000 m²/g specific surface area at pressures <100 bar.
- Perform high gravimetric and volumetric density analysis to demonstrate gravimetric density meeting or exceeding 11 wt% hydrogen at 77 K and 40 bar pressure. Assess in light of Hydrogen Storage Engineering Center of Excellence tank requirements.

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 Plan¹:

- (A) System Weight and Volume
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

This project is developing functionalized graphene materials to maximize hydrogen uptake and increase temperatures of operation. These materials are intended to meet the 2020 DOE hydrogen storage targets for high hydrogen gravimetric and volumetric capacity:

- System gravimetric capacity: 1.5 kWh/kg (4.5 wt% hydrogen)
- System volumetric capacity: 1.0 kWh/L (30 g hydrogen/L).

FY 2018 Accomplishments

- Incorporated transition metals toward enthalpy modification at nanoscale dimensions.
- Determined metal incorporation concentration via thermogravimetric analysis (TGA) and transmission electron microscopy (TEM).
- Sieverts measurements using Brunauer-Emmett-Teller (BET) apparatus showed

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

enhanced uptake with transition metal incorporation.

- Demonstrated isosteric heat enhancement from transition metal incorporation (10.8 to 14.4 kJ/mol).
- Thermally programmed desorption (TPD) analyses showed low temperature (140 K) and higher temperature (240 to 400 K) hydrogen release.

INTRODUCTION

One of the advantages of adsorbents as a storage medium is that dihydrogen retains its molecular form throughout the adsorption/desorption cycle, and the cycle requires minimal activation energy. The primary disadvantage of sorbents is that typical adsorption enthalpies are relatively weak compared to bond formation with chemical hydrogen or to interstitial atomic hydrogen in metal hydrides. Additionally, the van der Waals dimension of molecular hydrogen is large in comparison to atomic hydrogen, putting limits on the overall volumetric density that systems based on dihydrogen can achieve.

Graphene-based materials offer an excellent starting platform for hydrogen sorption owing to their high surface area for dihydrogen adsorption. The key step is to optimize functional groups on the graphene to maximize the volumetric density of dihydrogen adsorption. Part of the effort at Caltech is directed toward this optimization. While prior work on physisorbents has illustrated the importance of high surface area in achieving gravimetric uptakes of relevance to the program, volumetric densities have recently been recognized as a critical metric. Under many conditions, the nature of the adsorption process can still offer volumetric density advantages over the use of compressed gas storage, although not as high as intermetallic hydride densities. For dihydrogen that adsorbs onto a substrate, the London dispersion forces that can be regarded as transient dipoles in polarizable substances are a major contributor to physisorption processes. We are designing metal functionalizations for carbon surfaces that should optimize these attractive forces, enabling higher heats of adsorption, higher temperatures of operation, and higher capacities per surface area of material.

APPROACH

Previous work at Caltech has shown that alkali metal-intercalated graphites, which have pore dimensions similar to the graphene geometries we seek, can result in constant isosteric enthalpies of adsorption. These specialized structures have the advantage of electron back donation from the alkali metal to the graphitic planes, but these observations motivate the addition of metal atoms substitutionally in the graphene or on graphene surfaces. These local centers could increase both the isosteric heat of adsorption and the number of active sites for dihydrogen adsorption. We also note that for hydrogen on metal surfaces, adsorption and desorption typically occur above room temperature.

This project aims to promote high surface-packing density of hydrogen and high constant isosteric enthalpy in graphene and graphene-based materials. Specific key goals are to attain a high volumetric density of hydrogen, a near-constant heat of adsorption, rapid kinetics for adsorption and desorption, and long cycle life. We have altered the carbon surfaces by incorporating metal centers to increase the strength of the dispersion forces. We will continue to optimize the incorporation of these metal centers to gain better understanding of hydrogen physisorption and to reach technical targets for system gravimetric and volumetric capacity.

RESULTS

Efforts for the third phase of this project occurred in three primary areas: (1) down-selection of graphene synthesis approaches, (2) modification of graphene via metal functionalization demonstrating enhanced isosteric enthalpies and uptakes, and (3) hydrogen adsorption and desorption measurements demonstrating higher-temperature hydrogen release over a 240 to 400 K temperature range via TPD/residual gas analysis (RGA), consistent with the higher enthalpy evaluation.

This effort required down-selection of a number of graphene synthetic approaches given the discrepancies in the scientific literature, where high surface area graphene syntheses were purported to yield specific surface areas that were comparable to activated carbons. Unfortunately, the typical processing routes employed yielded material that was no different morphologically than activated carbon, as we could discern through optical and TEM studies. While problematic from the standpoint of fulfilling the metrics proposed for our third-year objectives, we directed our efforts to determining the efficacy of metal modification and hydrogen uptake enhancement.

A subset of metal-modified materials was described at the 2018 Annual Merit Review (ST120) including twelve Cu, eight Ni, three Co, three Zn, two Au, and three Ag metals that had been incorporated into carbon using metal salt solutions. Figure 1 shows TEM micrographs of some of these materials where, given the lapse of time between synthesis and analysis, the metal nanoparticles had oxidized but had retained their nanoscale dimensions. Experiments performed on the Cu-containing samples were subjected to static or flowing hydrogen gas as a reduction treatment before hydrogenation/dehydrogenation experiments were performed.

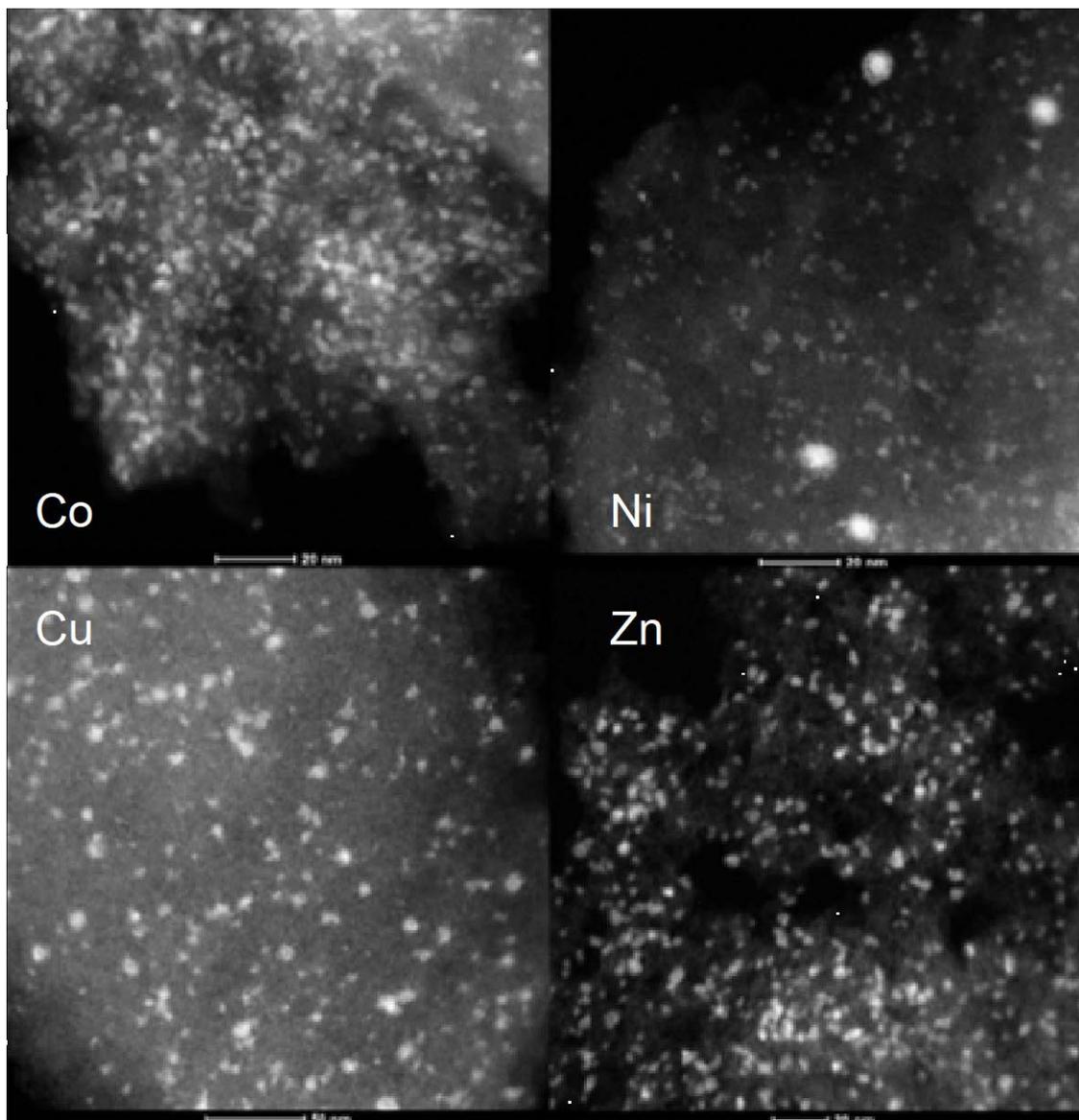


Figure 1. Transition metal incorporation showing nanoscale dimensions of the metal (oxidized during sample handling and transport to Pacific Northwest National Laboratory [PNNL]). Images courtesy of M. Bowden at PNNL.

X-ray fluorescence experiments were performed on these materials to establish the extent of metal loading; however, a baseline had to be established as the fluorescence unit had no capability for establishing direct carbon quantity comparison. An alternative technique was employed using TGA to quantify the initial metal mass fraction after the carbon has burned, leaving metal oxide. Several of these analyses are shown in Figure 2, comparing complete carbon mass loss for pure carbon samples to samples of metal-incorporated carbons.

The stability of the mass measurement at high temperatures provides a high level of confidence in the stability of this approach. Also of note is the small initial mass of material necessary for this type of analysis.

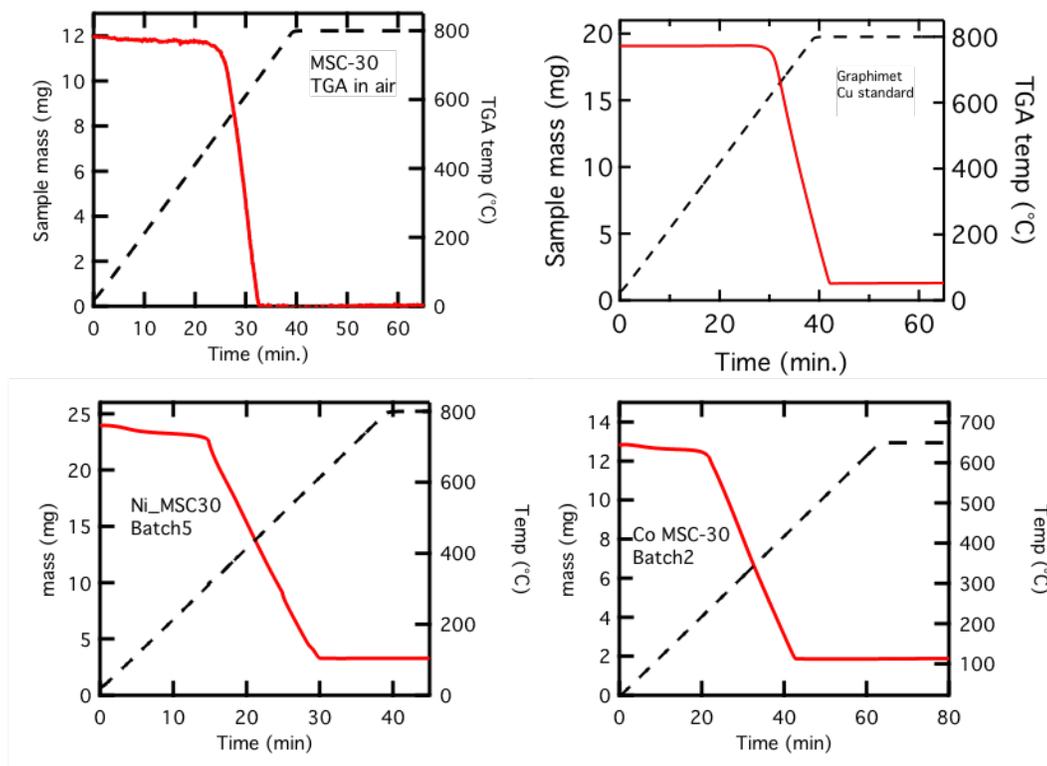


Figure 2. TGA results for the heating of pristine carbon (upper left) and metal-functionalized materials in air. Continuous heating of the samples to at least 650 °C in air causes complete loss of the carbon matrix, leaving behind fully oxidized metals. Metal-functionalized quantities were 1.1 wt% (2.5 at%) for the Ni-containing sample (lower left), 5.4 wt% Cu in a commercial “graphimmet” test sample (manufacturer specified 4.53%) (upper right), and 11 wt% (2.2 at%) Co in the lower right. Results can be normalized for quicker X-ray fluorescence analysis.

Our initial evaluation of the improvement to the Henry’s law “differential enthalpy of adsorption at zero coverage” follows that of Cole et al. [1]. By plotting k_H as a function of inverse temperature, for which k_H is defined as:

$$k_H H = \lim_{p \rightarrow 0} (n/p)$$

we can determine a -10.8 kJ value for the temperature range of 240 and 296 K and -14.4 kJ at the somewhat higher 319 K temperature. All of our previous work does indicate that higher temperatures have a higher enthalpy.

We initiated TPD measurements in collaboration with the National Renewable Energy Laboratory. Once it became clear that this would be a fruitful direction, we modified an RGA setup in the lab of David Boyd at Caltech in order to obtain higher throughput and minimize sample handling complications. This allowed us to take the reactor containing sample at 77 K directly from our Sieverts apparatus to the RGA setup in Boyd’s lab. Figure 3 shows baseline data for an unmodified carbon and nanoparticles of Cu only. A gas mixture of deuterium and hydrogen in the volume ratios noted in the figures was used to probe for isotope mixing. In the carbon-only sample, we observe physisorbed gas release only peaking at 140 K, and in the Cu nanoparticle-only sample we observe chemisorbed peaks only.

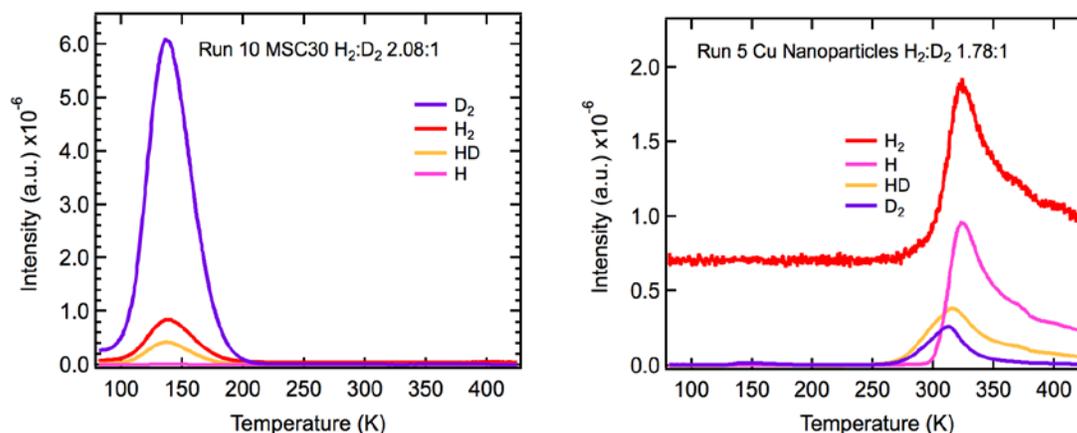


Figure 3. On left, pure MSC30-RGA traces of H₂, D₂, HD, and atomic H released ~140 K. On right, pure Cu nanoparticle-RGA traces of H₂, D₂, HD, and atomic H. Chemisorbed gas release is below 400 K. Ratio of H₂ to D₂ is slightly lower than that used in left figure data. A relatively large atomic H quantity is detected and HD formation is also evidenced → H₂ and D₂ dissociation.

Figure 4 shows a hydrogen BET isotherm from a Cu-modified sample, and the TPD RGA traces show a relatively larger quantity of chemisorbed hydrogen being released. There is also clear evidence of isotope mixing as the HD signal dominates the chemisorbed portion of the TPD data.

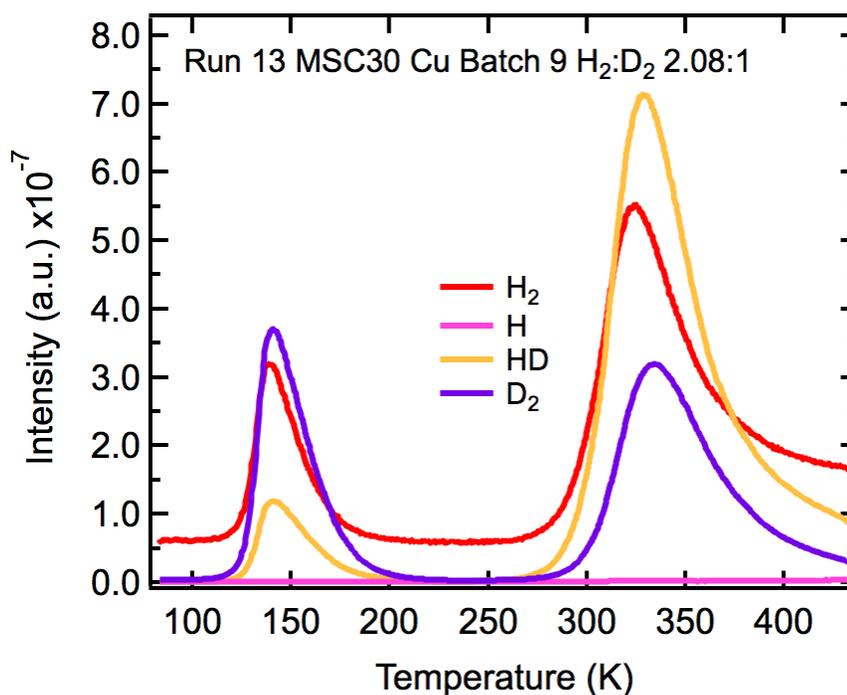


Figure 4. Cu on MSC30-RGA traces from the Batch 9 sample. The measurements used a 2:1 ratio of H₂ to D₂.

The results presented in Figure 4 show the desorption of hydrogen as a function of temperature for a Cu-modified sample. By inspection of the two temperature ranges over which hydrogen is released, it is clear that a large portion of the hydrogen is released in the higher temperature range, which is in fact the more technologically relevant regime. There are several phenomena that could be taking place to account for these

results. Some charge transfer from the metal to the carbon substrate could be taking place in addition to weak surface chemisorption of hydrogen onto the Cu surface, the latter as evidenced by isotope mixing. Given the enthalpy values we noted earlier, these observations give clear guidance for pursuing a combination of adsorbent/weak chemisorption studies.

CONCLUSIONS AND UPCOMING ACTIVITIES

As this project reaches the end of its third phase, several conclusions can be drawn:

- Relatively large quantities of graphene-based materials can be produced and functionalized with metals.
- Chemical functionalization of materials with metal salts can produce varying sizes and concentrations of metal clusters.
- TPD/RGA data between 77 K to above ambient temperature show an enhancement of hydrogen adsorption with Cu modification, indicating an increased enthalpy of adsorption in metal-functionalized materials and showing two distinct desorption regimes that we attribute to both physisorption and weak chemisorption. Enthalpy values of the higher temperature regime at 10 to >14 kJ/mole have been achieved and are in accordance with values required for technological applications.

Continuing goals for work over the no-cost extension phase of this project are to:

- Identify and quantify >40 g/L total adsorption, using multi-temperature analyses over 77 K to 400 K for isosteric heat validation >10 kJ/mole.
- Continue to pursue ≥ 1.5 wt% excess hydrogen per 500 m²/g in material with >3,000 m²/g specific surface area at pressures <100 bar and 77 K.
- Achieve net adsorption of ≥ 6 wt% hydrogen at any temperature or pressure, and achieve net adsorption of ≥ 1 wt% hydrogen at 30 bar and 300 K.
- Perform high gravimetric and volumetric density analysis to demonstrate gravimetric density meeting or exceeding 11 wt% hydrogen and volumetric capacities exceeding 40 g/L total at 77 K and 40 bar pressure.

REFERENCES

1. J.H. Cole, D.H. Everett, C.T. Marshall, A.R. Paniego, J.C. Powl and F. Rodriguez-Reinoso, "Thermodynamics of the High Temperature Adsorption of some Permanent Gases by Porous Carbons," *J. Chem. Soc. Faraday Trans. 1* 70 (1974): 2154.