

## IV.C.8 Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

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### Overall Objectives

- Develop a carbon-based, functionalized material prepared with new substrates (graphene) or old (exfoliated graphite) to maximize capacity for hydrogen physisorption at moderate temperatures.
- Understand how far hydrogen physisorption can extend beyond present capabilities with carbon materials.
- Demonstrate a near-constant isosteric heat of adsorption, excellent kinetics, and long cycle life.

### Fiscal Year (FY) 2016 Objectives

- Develop Sieverts method for rapid screening of materials that is comparable to full isotherms at 77 K and 87 K for agreement to within 5%.
- Demonstrate functionalization of graphene with metal clusters <1 nm.
- Synthesize graphene and demonstrate retention of 80% of as-prepared surface area after compression to bulk density of 0.5 to 0.7 gm/cc.
- Meet or exceed present capabilities of carbon sorbents before functionalization.

### 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:

- (A) System Weight and Volume
- (C) Efficiency
- (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 with the goal to meet the DOE hydrogen storage capacity targets.

- System gravimetric capacity: 1.8 kWh/kg
- System volumetric capacity: 1.3 kWh/L

### FY 2016 Accomplishments

- Prepared graphene oxide, microwave exfoliated graphene oxide (meGO), and as-activated graphene at Caltech, achieving a Brunauer–Emmett–Teller (BET) specific surface area of 2,640 m<sup>2</sup>/g, close to the theoretical value of 2,630 m<sup>2</sup>/g for a single graphene sheet.
- Improved density of as-activated graphene from a tap density of <0.33 g/cc to 0.59 g/cc while retaining 80% of the initial surface area.
- Demonstrated functionalization of graphene with Au and Cu clusters <1 nm in diameter.
- Developed a rapid turnaround Sieverts method for screening materials without the need to collect full isotherms.



### 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 for maximizing the volumetric density of dihydrogen sorption. Part of the effort at Caltech is directed toward this optimization. While prior work in the area of 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, regarded as transient dipoles in polarizable substances, are a major contributor to physisorption processes, and we are designing materials to optimize them.

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

## APPROACH

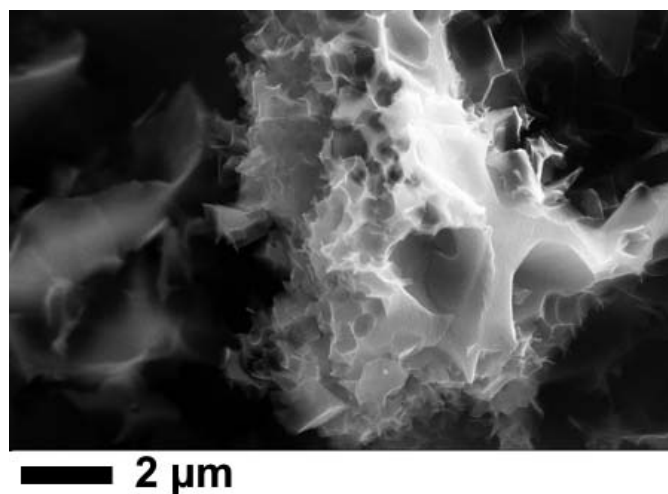
The focus of this project is to functionalize newly developed graphene materials to maximize hydrogen uptake. Specific key goals are to attain a high volumetric density of hydrogen, a near-constant heat of adsorption, rapid kinetics for adsorption and desorption, and long cycle life. The materials will rely on physisorption of hydrogen onto surfaces, or into internal pores. Given that metal centers have proved successful for increasing the local hydrogen density in other materials such as coordination polymer structures, we plan to alter surfaces or incorporate chemical center substituents to increase the strength of the dispersion forces.

## RESULTS

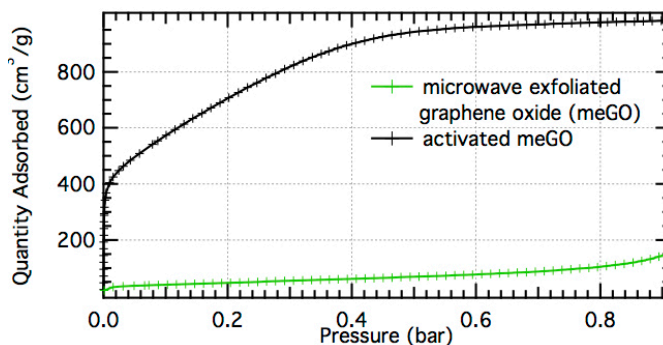
Efforts for the first phase of this project occurred in three primary areas: (1) synthesis of graphene and graphene oxide materials, (2) functionalization of graphene with metal nanoclusters, and (3) hydrogen adsorption measurements.

Synthesis efforts have yielded bulk quantities ( $>1$  g) of high purity graphine oxide and meGO as characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman, and BET. An activation route employed to modify the meGO resulted in as-activated graphene with a BET specific surface area of  $2,640$   $\text{m}^2/\text{g}$ . This surface area is within 5% of the theoretical surface for graphene of  $2,630$   $\text{m}^2/\text{g}$ , and represents a 15X increase in surface area over meGO. The complex, three-dimensional framework of the as-activated graphene is seen in the SEM image in Figure 1. The vast improvement in the surface area as determined with nitrogen BET is shown in Figure 2 where the meGO (green curve) has a surface area of  $167$   $\text{m}^2/\text{g}$  while the activated meGO (black curve) reaches  $2,640$   $\text{m}^2/\text{g}$ . These results position us to achieve second phase milestones including scale-up of the synthetic process to 300 mg quantities and measure changes in specific surface area and hydrogen adsorption capacity resulting from plasma etching.

Maximization of volumetric density is now recognized as a key metric in gauging the merits of an adsorbent. Unlike



**FIGURE 1.** Morphology of the high surface area, as-activated graphene material imaged with SEM



**FIGURE 2.** Comparison of the  $\text{N}_2$  adsorption of the meGO and as-activated graphene shows a 15X increase in surface area

three-dimensional structures, two-dimensional graphene can withstand mechanical compression in a way that can preserve a substantial fraction of the surface area without loss due to the collapse of a “framework.” We have successfully achieved our initial target to attain properties similar to that of a polyether ether ketone-based activated carbon. We have completed compression studies on as-activated graphene and MSC-30, compressing these materials to densities of 0.5 g/cc and 0.59 g/cc, respectively. As shown in Figure 3, the materials retained 85% and 80% of their BET specific surface areas, respectively. We note that 0.5–0.7 g/cc in an idealized structure would correspond to the removal of two or three planes of graphite in a graphitic structure and would provide the appropriate configuration to maximize the volumetric density of hydrogen consistent with retaining a practical gravimetric density. BET surface area analysis also revealed that in both materials, meso- and macro-pore surface areas were lost during compression, resulting in the overall loss of surface area, but micro-pore surfaces and micro-pore volume have increased from what were originally meso- and macro-pore volumes.

Our preliminary volumetric analyses, absent a full-scale engineering analysis that would include the storage tank and associated balance of plant components, indicates that we met our year one decision criteria. These criteria required meeting or exceeding present capabilities of carbons sorbents with 35 g/L total adsorption at 77 K and pressure <100 bar. Initial analysis of our as-activated graphene indicates we can achieve 35 g/L at 77 K and 84 bar. The assumptions made in this calculation are outlined in our 2016 go/no-go report to DOE.

Functionalization of the graphene and graphene-based carbons is at the core of our plan to reach DOE hydrogen storage targets for high volumetric density of hydrogen. We plan to incorporate metal substituents to increase the strength of the dispersion forces. In the first phase of the project, we demonstrated the deposition of Au and Cu metal nanoclusters <1 nm by both chemical and plasma deposition routes. Figure 4 shows a dark field TEM image of Cu nanoclusters on graphene. The chemical route used to deposit the Cu

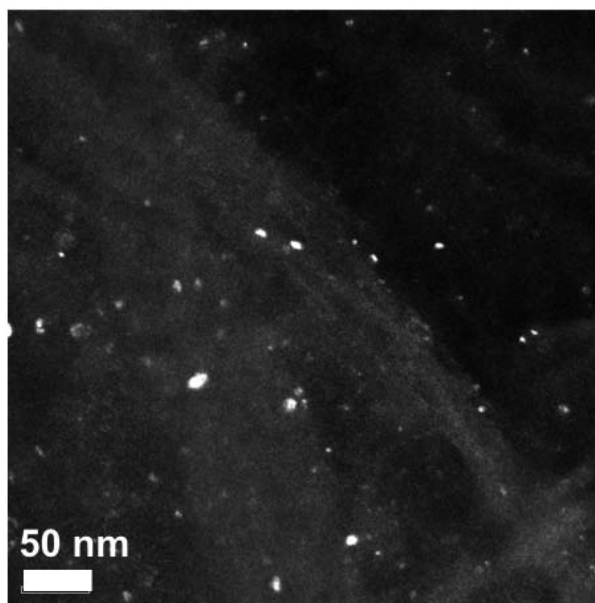


FIGURE 4. TEM dark field image of graphene functionalized with Cu nanoclusters (appearing in bright white regions)

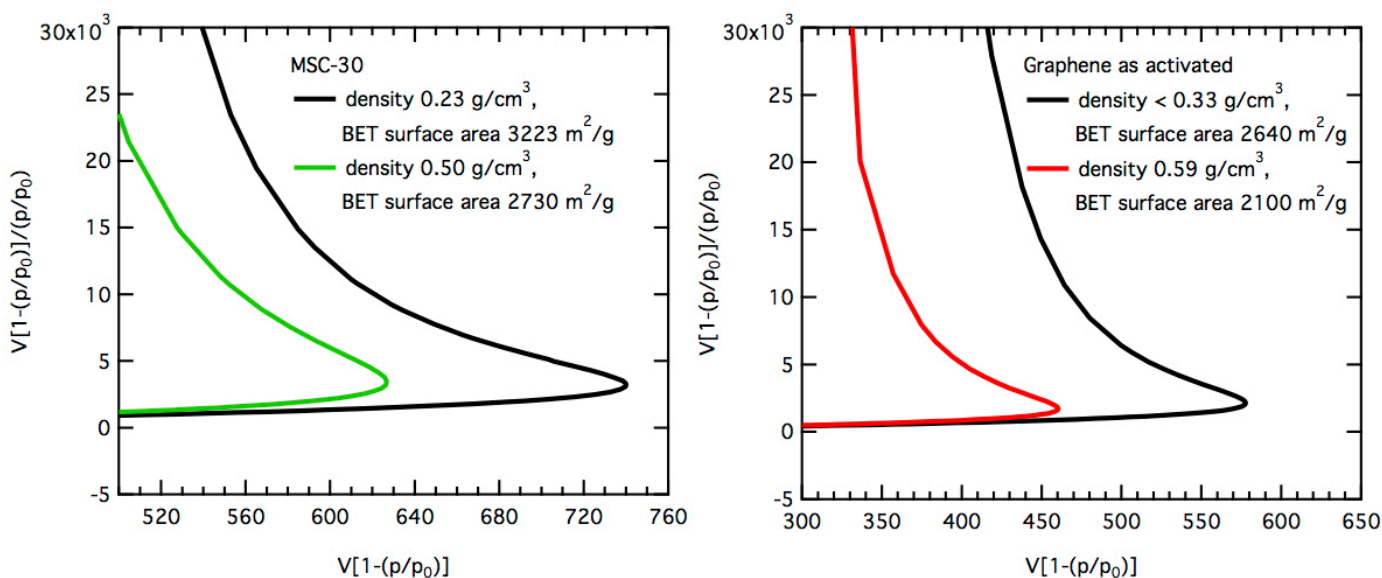


FIGURE 3. Compression tests on two materials demonstrate retention of >80% of initial BET surface area after densification

particles, which appear white in the image, produced some large clusters but a majority <1 nm, as evidenced from the small white dots. These results position us to achieve our second phase milestone of depositing sub-nanometer clusters of metal atoms onto carbon materials while reducing surface area by <10%, improving average isosteric heat, and achieving  $\geq 1.3$  wt% excess  $H_2$  per 500  $m^2/g$  of material.

Hydrogen adsorption measurements using the Sieverts method are critical to characterization of the materials we develop. The long turnaround time for collection of full isotherms was identified as a potential bottleneck in our development and assessment of new materials, and the first phase of the project included milestones to mitigate this problem. A second Sieverts apparatus on long-term loan from Jet Propulsion Laboratory was installed in new lab space and is now fully commissioned. A “Rapid Sieverts” screening method was developed to obtain key data in shorter times by measuring a single data point at 77 K and 20 bar. This decreases data acquisition time by a factor of three, and provides the means to quickly assess whether full isotherm data should be collected. We tested this approach by comparing the Rapid Sieverts method to full multipoint isotherm data on several samples and the agreement is excellent. Hydrogen adsorption measurements plays a key role in the second phase of the project, and these first phase achievements position us to achieve goals for characterization of materials developed in phase two.

## CONCLUSIONS AND FUTURE DIRECTIONS

Although the project is still in early stages, several conclusions can be drawn.

- Graphene can be functionalized with small metal clusters with sizes below 1 nm, validating the proposed approach to measure hydrogen adsorption after introduction of these sites.
- High-surface area graphene-based materials have been synthesized and compressed to 0.59 g/cc, retaining >80% of original surface area and achieving an estimated 35 g/L at 77 K and 84 bar.
- Methods for rapid hydrogen adsorption analysis were developed to reduce the time required for a detailed work-up.

Goals for work in the second phase of the project are:

- Scale-up of synthetic processes to 300 mg quantities with gravimetric and volumetric capacities within 5% of the performance observed in small batch material.
- Use of oxygen plasma etching to induce 1–2 nm pores in graphene sheet structures and demonstrate >10% increase in BET surface area and to sorption properties.
- Deposition of sub-nanometer clusters of metal atoms onto carbon materials while reducing surface area by <10%.
- Improvement of average isosteric heat and  $\geq 1.3$  wt% excess  $H_2$  per 500  $m^2/g$  in material with >3,000  $m^2/g$  surface area and 35 g/L total volumetric capacity at pressures less than 100 bar and 77 K.