Naval Research Laboratory

Washington, DC 20375-5320

NRL/MR/6360--19-9899

Hydrogenated Graphite for Solid-State Hydrogen Storage: Evaluation of Bulk Impurities and Post-Synthetic Purification Strategies

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August 5, 2019

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 05-08-2019	**2. REPORT TYPE** NRL Memorandum Report	**3. DATES COVERED** *(From - To)* 07/11/2017 - 04/10/2019

4. TITLE AND SUBTITLE

Hydrogenated Graphite for Solid-State Hydrogen Storage: Evaluation of Bulk Impurities and Post-Synthetic Purification Strategies

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62123N

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER
UW-123-001

5f. WORK UNIT NUMBER
6846

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/MR/6360--19-9899

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR / MONITOR'S ACRONYM(S)

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

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This work was performed by James Morse while under a Karles Fellowship

14. ABSTRACT

The major challenge in the application of hydrogen powered fuel cells for military applications, is the safe and effective high-density storage of the hydrogen. To this end, NRL has demonstrated for the first time the large-scale synthesis and characterization of chemically hydrogenated graphite in order to quantify its bulk hydrogen storage capacity and understand its thermal decomposition under relevant operating conditions. Post-synthetic purification strategies were developed to reduce residual alkali-based byproducts persisting from the synthesis of the chemically hydrogenated graphite. Multi-gram quantities of hydrogenated graphite samples were quantitatively analyzed using a high pressure hydrogen generator. Under an evacuated atmosphere at 550 °C, hydrogenated graphite was found to generate a gas mixture composed of 92% H2, which was purified using a commercial carbon filter. The H2 gas generated corresponded to an H2 storage capacity of 4.26 wt. %.

15. SUBJECT TERMS

Hydrogenated graphite Solid-state hydrogen storage

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			James R. Morse
Unclassified Unlimited	Unclassified Unlimited	Unclassified Unlimited	Unclassified Unlimited	23	**19b. TELEPHONE NUMBER** *(include area code)* (202) 404-3418

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EXECUTIVE SUMMARY

The major challenge in the application of hydrogen powered fuel cells for military applications, is the safe and effective high-density storage of the hydrogen. To this end, NRL has demonstrated for the first time the large-scale synthesis and characterization of chemically hydrogenated graphite in order to quantify its bulk hydrogen storage capacity and understand its thermal decomposition under relevant operating conditions.

Post-synthetic purification strategies were developed to reduce residual alkali-based byproducts persisting from the synthesis of the chemically hydrogenated graphite. Multi-gram quantities of hydrogenated graphite samples were quantitatively analyzed using a high pressure hydrogen generator. Under an evacuated atmosphere at 550 °C, hydrogenated graphite was found to generate a gas mixture composed of 92% H_2, that was purified using a commercial carbon filter. The H_2 gas generated corresponded to an H_2 storage capacity of 4.26 wt. %, which is 55% of the expected value for a theoretically pristine sample. While improvements to the bulk synthetic protocol are expected to further increase the H_2 storage capacity of this material, the results presented demonstrate multi-gram quantities of hydrogenated graphite can be used to safely generate practical quantities of H_2 gas on demand. These results are the first step towards the development of an inexpensive, high-density, user friendly, safe, pressure-tolerant solid hydrogen storage material as a game-changing energy solution for military applications.

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1.0 BACKGROUND

Hydrogen fuel cells are particularly attractive power sources for unmanned underwater vehicles (UUV's) as they can deliver greater power densities than current state of the art lithium ion batteries,[1–3] thus allowing for increased mission durations. However, traditional pressurized hydrogen storage is non-ideal for UUV application, as its volumetric energy storage density is too low, making its employment prohibitively bulky and heavy. Additionally, the consumption of pressurized hydrogen gas would cause significant changes to the vehicle's buoyancy during deployment, introducing operational challenges. Considerable effort has been focused on developing alternative hydrogen storage technologies in the hopes of improving energy density, however, this research has yet to yield functional alternatives.[4–6] The U.S. Naval Research Laboratory (NRL) is currently investigating solid-state hydrogen storage technologies as an alternative to safely and efficiently store hydrogen for on demand use to power underwater systems. Recently, our group has demonstrated the controllable release of hydrogen from chemically hydrogenated graphite, which was synthesized in house, at a large and economically feasible scale.[3]

Chemically hydrogenated graphite is stable in air up to temperatures of about 400 °C, above which, it thermally decomposes to liberate gaseous H_2.[3,7–9] Fully hydrogenated graphite, graphane $(CH)_n$, possesses a theoretical hydrogen storage capacity of 7.7 wt.%, which is well above the U.S. Department of Energy's 2020 target for portable power applications (4.5 wt. %).[10] In addition, the hydrogen stored within graphane possesses a volumetric energy density of 0.17 kWh L^{-1}, ten times greater than hydrogen gas pressurized to 3,000 PSI.[3,11] Like graphene, chemically pristine graphane is challenging to isolate, however, bulk graphite can be chemically hydrogenated to yield a chemically similar product with hydrogen loadings reported to approach the theoretical limit of graphane.[12,13] The large hydrogen density (on both a per mass and per volume basis), coupled with the straightforward release of H_2 by thermal triggering, makes hydrogenated graphite a promising material for high density solid-state hydrogen storage.[14,15]

To date, the study of hydrogenated graphite (and similar carbon allotropes) has been almost exclusively academic in nature. Published syntheses describe yields on the sub-gram scale, and previous studies have only demonstrated (albeit promising) "proof of concepts".[7–9,12,13,16,17] In order for this material to be realized as a practical hydrogen storage medium, large-scale syntheses need to be optimized so that prototype vehicles can be designed and tested. Perhaps even more importantly, quality control protocols and post synthetic treatments should be developed to identify and eliminate residual byproducts and contaminates, as any potential impurities lower the maximum hydrogen storage capacity of the material and may also pose a hazard to fuel cell operation.

In this work, we synthesize hydrogenated graphite in multi-gram quantities using an adapted Birch Reduction, and then critically characterize the material in order to identify the source and nature of deleterious contaminants. We go on to demonstrate that these hydrogenated materials can be post-synthetically treated to reduce contaminating species, thus improving the hydrogen storage capacity of the material and making it a more viable form of energy storage. Finally, we demonstrate the large-scale and quantifiable H_2 generation from hydrogenated graphite using a high-pressure reaction vessel. Post synthetic treatment was found to improve the overall purity of the hydrogenated graphite, however, it did not completely eliminate the evolution of unwanted gases, such as NH_3, from the material. Accordingly, we recommend purification of the gas stream before fuel cell operation. The insights

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Manuscript approved April 17, 2019.

presented in this work will aid in the realization of carbon-based hydrogen storage technologies with direct applications for U.S. Naval systems.

2.0 OBJECTIVE

The objective of this work is to enable the development of procedures to safely and economically generate kilogram quantities of high purity hydrogenated graphite, which may serve as a practical solid-state hydrogen storage medium. To accomplish this objective we test and characterize hydrogenated graphite under working conditions to identify the H_2 storage capacity of the material, as well as any deleterious impurities. We subsequently describe the development of post-synthetic protocols to purify the hydrogenated graphite and minimize unwanted contaminates.

3.0 EXPERIMENTAL

3.1 Materials

Unless otherwise noted, all materials were used as purchased. Graphite (powder, <20 µm), nitric acid (ACS reagent, 70%), acetic acid (ACS reagent, > 99.7%), sulfuric acid (ACS reagent, 95%), and phosphoric acid (85 wt. % in H_2O) were all purchased from Sigma Aldrich. Methanol (certified ACS), hexanes (certified ACS), dichlormethane (certified ACS), and hydrochloric acid (certified ACS plus) were purchased from Fischer Scientific. Lithium (granules, 99% metals basis) was purchased from Alpha Aesar. Liquefied ammonia (anhydrous) was purchased from Matheson.

3.2 Large-Scale Synthesis of Hydrogenated Graphite

Graphite and similar carbon allotropes can be hydrogenated via wet chemical means using an adapted "Birch Reduction".[7,9,12,17] Briefly, graphite is suspended in liquid ammonia under an inert atmosphere, to which an alkali metal (Li, Na, K, etc.) is then dissolved. The liquid ammonia serves to "solvate" electrons donated from the dissolved metal, which then act to reduce the suspended graphite. A protic solvent, such as water or an alcohol, is then added to the solution to function as a "proton donor", which hydrogenates the reduced carbon lattice. Once complete, the reaction is warmed to room temperature to allow the ammonia to evaporate, leaving behind the hydrogenated graphite, along with any remaining byproducts such as residual salts. The cryogenic temperatures and extreme reactivity of the chemical precursors require great caution be exercised during the synthesis of this material at any scale.

To generate multi-gram quantities of hydrogenated graphite, the Birch Reduction was adapted and scaled up. About 1.5 L of ammonia was condensed into a 3 L five arm flask, submerged in a dry ice acetone bath (~ -76 °C) under a flowing nitrogen (N_2) atmosphere. A condensing column was also filled with dry ice/ acetone and included in the reaction setup, along with a Qsonica Q700 (120V) sonication horn to agitate the solution as needed. The reaction was mechanically stirred at about 60 rpm. Approximately 75 g of graphite was added, and then the solution was sonicated over the course of 2 hours, in an attempt to exfoliate and better suspend the graphite. After sonication, 55 g of Li pellets were added, and the solution was again sonicated for 2 hours. 0.5 L of methanol was then added to the reaction via a syringe pump at a rate of 1 mL min^{-1} to hydrogenate the reduced graphite suspension. The reaction was then left for approximately 12 hours to warm to room temperature to allow the NH_3 to evaporate. The following day, the resulting solid material was suspended in a solution of water to which concentrated hydrochloric acid was added until the solution was measured to be slightly acidic (pH ~6). The suspended hydrogenated graphite was then isolated via vacuum filtration, and washed with deionized water 3 times. The resulting black powder was dried in a vacuum oven at 200 °C for about 24 hours.

3.3 Post Synthetic Treatment of Hydrogenated Graphite

3.3.1 Acid washing

10 g of hydrogenated graphite was added to 0.8 L concentrated hydrochloric acid (HCl) and stirred overnight. The following day, the solution was diluted with 8 L deionized water and dried via vacuum filtration. The material was rinsed with deionized water two more times. The eluate of the final rinse was tested with pH paper and found to be neutral, confirming no substantial quantity of HCl persisted in the washed material.

To compare the influence of acid strength, the same acid washing procedure outlined above was performed using 10 g of hydrogenated graphite and 0.8L of 1M HCl.

To test the performance of other acid solutions, the same procedures above were followed at a smaller scale, with nitric, phosphoric, sulfuric, and acetic acids.

3.3.2 Liquid-liquid extraction

5 g hydrogenated graphite was treated with concentrated HCl as described in section 3.3.1, and then added to a separatory funnel containing 0.7 L deionized water and 0.7 L hexanes. The funnel was capped, then shaken vigorously and left overnight to allow phase separation to occur. The following day, the hexane fraction was isolated. It should be noted that significant quantities of hydrogenated graphite persisted in the aqueous phase, which made up the bottom half of the biphasic mixture.

Liquid-liquid extraction using a dichlormethane (DCM)-H_2O mixture was also evaluated under identical conditions. Using this DCM-H_2O mixture, all graphite partitioned into the DCM phase, which made up the bottom half of the biphasic mixture. With the organic phase existing in the bottom half of the biphasic mixture, all solid material was observed to partition into the DCM. This made isolation of the hydrogenated graphite significantly less challenging.

3.3.3 Sonication

10 g hydrogenated graphite was added to 1.5 L deionized water which was stirred and agitated via a horn sonicator (Qsonica Q700) for 1 hour. The hydrogenated graphite was then isolated via a DCM-H_2O liquid-liquid extraction as described in section 3.3.2.

3.3.4 Thermal Ripening

5 g of hydrogenated graphite was added to a high pressure reaction vessel (Parr instruments: 4760 HP/HT), which was then sealed under either a) ambient atmosphere, or b) 300 PSI H_2. The system was then heated to 550 °C and held for 2 hours, after which it was cooled to room temperature. The material was then treated with concentrated HCl and washed with H_2O via vacuum filtration as described in section 3.3.1.

3.4 Characterization

3.4.1 Thermogravimetric Analysis-Mass Spectrometry

Thermogravimetric analysis coupled with mass spectrometry (TGA-MS) was used to characterize the thermal decomposition behavior of hydrogenated graphite samples. The TGA-MS experimental setup consisted of a Q500 TGA (TA Instruments) connected to a HPR-20 benchtop mass spectrometer (Hiden Analytical). Approximately 15 mg of sample was added to an alumina boat, which was then purged with Ar gas for 90 minutes at a flow rate of 200 mL min^{-1} at room temperature, and then heated to 975 °C at a rate of 5 °C min^{-1}. Volatile products generated in the TGA furnace were initially introduced to the mass spectrometer operating at 70 eV using a scanning range of 2 to 120 *m/z* to determine the most prominent species. Higher resolution MS runs were then performed by monitoring the most common ions (*m/z* 2, 12, 14, 16, 17, 18, 28, 32, and 44). An ionization of 16 eV was used to detect *m/z* 16 in order to differentiate the signature from H_2O and NH_3 contributions.[18] All other all other ions were detected using an ionization energy of 70 eV.

Calibration of the mass spectrometer was achieved using response factor values determined from a blend of N_2, CO_2, CO, H_2 and CH_4 of known composition. MS calibration for H_2O and NH_3 vapors were performed using an N_2 stream saturated in the respective vapors, with response factors calculated using tabulated vapor pressures of the respective gases.[19]

3.4.2 X-Ray Diffraction

Measurements were performed on a Rigaku Smartlab X-ray diffractometer using Cu Kα monochromatized radiation operated at 44 kV and 40 mA at room temperature over the range of 5-90° 2θ. X-ray diffraction patterns for the catalysts were referenced to reported patterns from the ICDD database.

3.4.3 Large-Scale H_2 Liberation

The quantity and composition of gaseous species generated from the thermal decomposition of hydrogenated graphite samples were identified using a 0.6 L Parr pressure reactor (Parr 4760 HP/HT) plumbed to the calibrated mass spectrometer. Figure 6 provides a box diagram of the experimental setup both with and without a carbon filter to purify the evolved gas.

In a typical experiment, a known mass of hydrogenated graphite was added to the reactor, which was then sealed. The atmosphere of the reactor was evacuated using a connected vacuum pump. The system was then held under vacuum at either room temperature or 325 °C and held for 0.5 hours, to remove any lower boiling point impurities from the sample. After 0.5 hours, the valve connecting the vacuum pump was closed, isolating the reactor. The reactor was then heated to 550 °C (or 600 °C where noted), and held for 15 minutes to allow the pressure within the reactor to stabilize. The pressure of the reactor was recorded, and assumed to be due entirely the gas evolved from the sample after the vacuum source was closed. Assuming ideal gas behavior, the quantity of generated gas was calculated using a volume of 0.6 L, and the recorded temperature and pressure of the reaction vessel. To characterize the composition of the gas within the reactor, the atmosphere of the system was vented to the calibrated mass spectrometer at a controlled rate using a mass flow controller (Brooks SLA5850).

4.0 RESULTS AND DISSCUSSION

4.1 Characterization of Hydrogenated Graphite

The chemically bound hydrogen of hydrogenated graphite (HG) can be thermally liberated at temperatures above 400 °C, yielding H_2 gas. To better understand the practicality of this material for hydrogen storage applications, multi-gram quantities of hydrogenated graphite were synthesized, characterized for impurities, and then evaluated for H_2 storage applications. Following the large-scale

Birch reduction detailed in Section 3.2, the as synthesized hydrogenated graphite (*as synthesized-HG*) was heated to 200 °C in a vacuum oven overnight to remove any absorbed solvent and low boiling point impurities. Thermogravemetric analysis coupled with mass spectrometry (TGA-MS) was then used to characterize the decomposition of the hydrogenated graphite when heated under an Ar atmosphere. Unless otherwise noted, all TGA-MS runs were performed by purging the samples under flowing Ar at room temperature for 90 minutes, then heated to 975 °C under Ar flow at a rate of 5 $°C\ min^{-1}$. Figure 1a shows the mass loss profile for the *as synthesized-HG*, overlapped with the significant mass fragments detected during the TGA-MS run. About 2.5% of the sample's initial mass is lost during the 90 min purge, before sampling with the mass spectrometer was initiated. Further mass loss of about 2% is observed as the sample temperature approaches 70 °C, which appears to correspond to the evaporation of water (*m/z* 18). No further mass loss was observed until temperatures exceeded 200 °C. The evaporation of water from the sample is notable, as the sample was heated to 200 °C under vacuum prior to TGA-MS analysis. This suggests the *as synthesized-HG* sample reabsorbed water from ambient atmosphere after the heated vacuum treatment.

Above 200 °C, further mass loss is observed for the hydrogenated graphite sample. Before the evolution of H_2, mass fragments corresponding to CH_4, NH_3, H_2O and CO_2 (*m/z* 16, 17, 18, and 44, respectively) are observed in the temperature range of 200-375 °C. We attribute this to other chemically bound species on the graphite lattice, such as oxygen and nitrogen functionalities, which are expected to decompose in this temperature range.[20,21] In the temperature range between 375 to 575 °C, the mass fragment corresponding to H_2 (*m/z* 2) dominates the mass spectrum, although trace signals corresponding to CH_4 NH_3, H_2O and CO_2 are also still observed. Above 600 °C, minimal H_2 is detected, but significant mass loss is observed. In this temperature range, mass fractions corresponding to CO and CO_2 species are detected, however, the signal intensities for these species alone are not proportionate to the large mass loss observed. We hypothesize the majority of mass lost in this range is due to high boiling point contaminate species evolving from the sample and subsequently depositing within the instrument before reaching the mass spectrometer. The origin of this high temperature mass loss will be addressed later in this manuscript.

Analysis of Figure 1a demonstrates that species other than fully hydrogenated graphite are present in the *as synthesized-HG* sample, which decompose or are otherwise liberated from the sample upon heating. The presence of such contaminates not only reduces the overall hydrogen storage capacity of the synthesized material, but also promotes the evolution of gaseous species which are known to degrade fuel cell performance, specifically NH_3 and CO.[22–24] Accordingly, if hydrogenated graphite is to be employed for hydrogen storage applications, care must be taken to purify these contaminates.

In an effort to remove the chemical functionalities that thermally decompose at temperatures below H_2 liberation, the *as synthesized-HG* was heated to 350 °C under vacuum, held for 1 hour, and then cooled to room temperature. Figure 1b shows the TGA-MS mass loss profile and overlapped mass fragments for this sample. Again, about 5% of the sample's mass is lost once temperatures reach about 70 °C, corresponding to the evaporation of water from the sample. Beyond this, no mass loss is observed below 350 °C, and above 350 °C the decomposition profile is commensurate with the profile of the *as synthesized-HG* in Figure 1a. This result demonstrates vacuum heating as a straight forward and effective method to remove at least some fraction of impurities from hydrogenated graphite. For this reason, all subsequent TGA-MS characterization was performed on samples treated at 350 °C under vacuum.

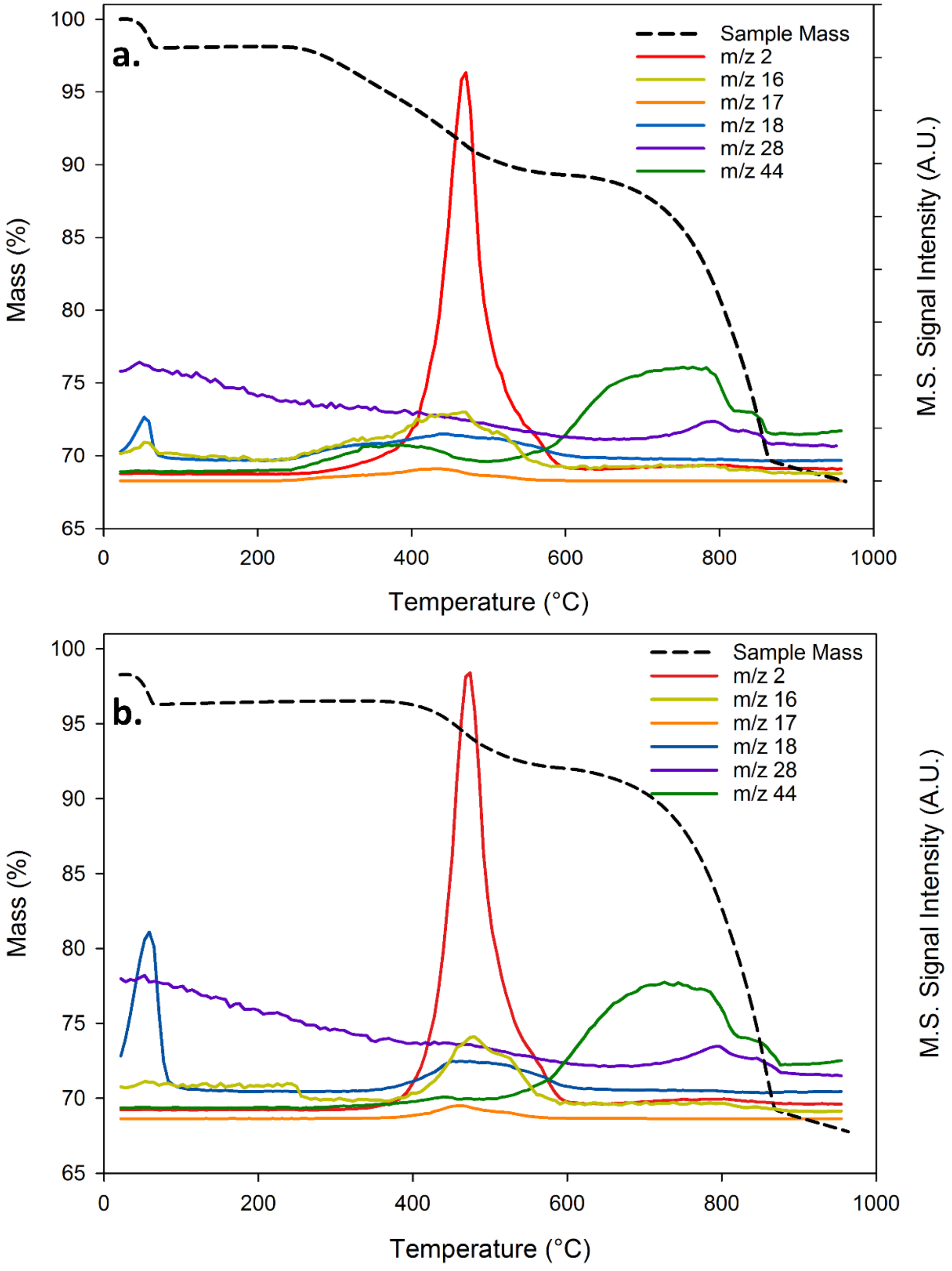

Figure 1. TGA profile with select MS signals for *as synthesized-HG* preheated to a) 200 °C and b) 350 °C.

To further characterize the hydrogenated graphite, X-ray diffraction was performed on the graphite starting material, the *as synthesized-HG* sample, and the *as synthesized-HG* sample after it was held under vacuum at 550 °C for 1h (*HG-550 °C*). Figure 2 shows the corresponding X-ray diffraction patterns for these three samples. The most notable difference between the graphite precursor and the HG sample is the characteristic shift and broadening of the (002) reflection from 26.6 to 18.8° 2θ, indicating an increase in the d-spacing between the carbon sheets due to hydrogenation of the carbon lattice.[12,25] The *as synthesized-HG* sample still exhibits a reflection at 26.6° 2θ, indicating non-hydrogenated graphite portions are still present after the large-scale synthesis of the hydrogenated graphite (optimization studies for the large-scale synthesis of HG are currently in progress and will be reported in a subsequent manuscript). Between the range of 29-41° 2θ, broad and unresolved peaks can be observed for the *as synthesized-HG* sample, which cannot be attributed to any known reflections for graphite or hydrogenated graphite. For the *HG-550°C* sample, the (002) reflection is exclusively observed at 26.6° 2θ, demonstrating complete removal of hydrogen due to thermal liberation. In addition, the *HG-550 °C* sample also exhibits sharper peaks within the range of 29-41° 2θ, which fit known patterns corresponding to LiCl, LiOH·(H2O) and Li_2CO_3 crystal phases. This result demonstrates significant Li based contaminants persisted after the synthesis of the HG material. The increased signal intensity of these reflections in the *HG-550 °C* sample is most likely due to thermally induced crystallization of less crystalline Li contaminants in the *as synthesized-HG* sample.

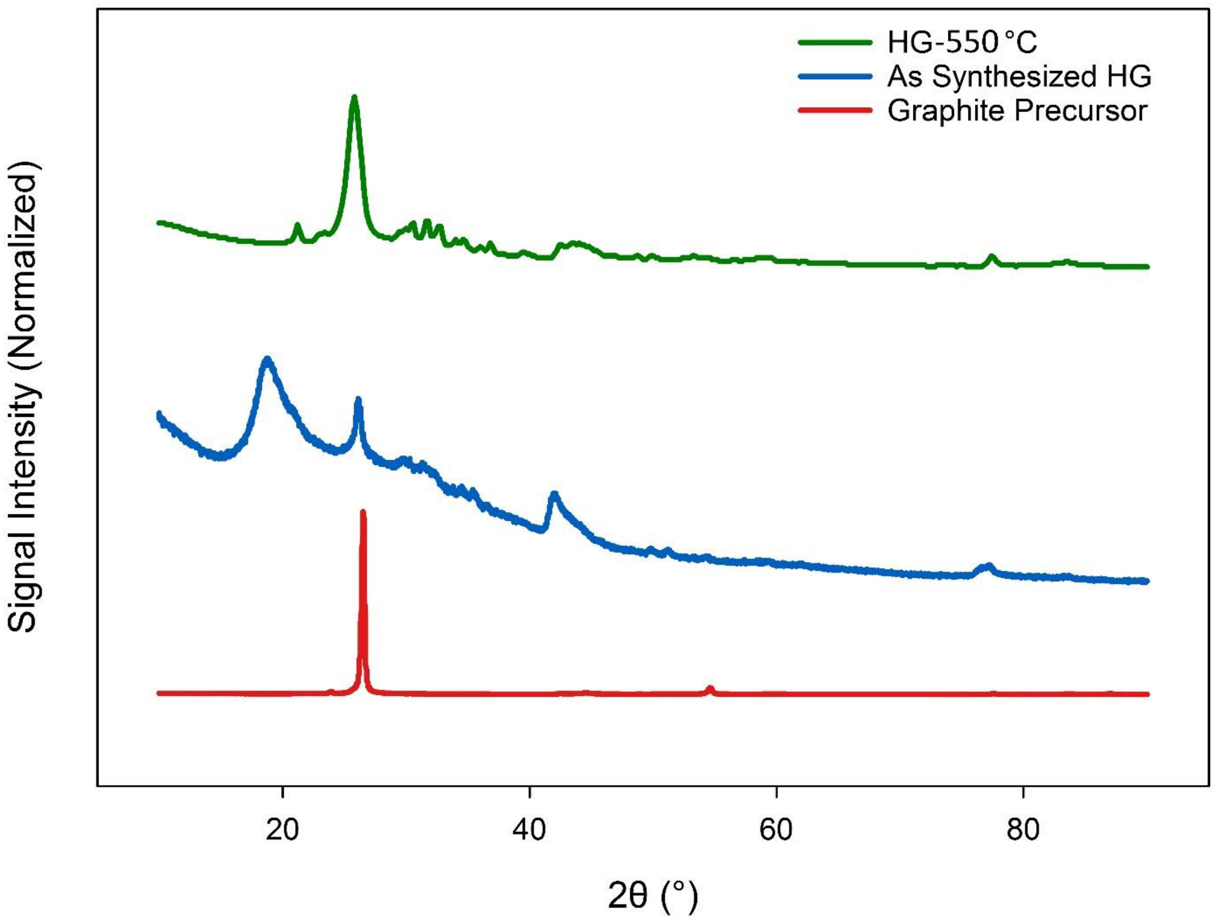

Figure 2. X-ray diffraction patterns for (red) graphite precursor, (blue) *as synthesized-HG*, and (green) HG-550 °C.

The presence of Li-based contaminates in the *as synthesized-HG* may be used to rationalize the high temperature (> 600 °C) TGA profile of the material described in Figures 1a and 1b. Although we cannot unambiguously characterize the Li species in the *as synthesized-HG* by XRD, we speculate the major Li components to be some mixture of Li_2CO_3, LiCl, and $LiOH{\cdot}(H_2O)$ leftover as a byproduct of the Birch Reduction. Previous authors have demonstrated that, when mixed with graphite, LiOH converts to Li_2CO_3 at temperatures above 400 °C.[26] Furthermore, additional TGA studies have demonstrated graphite/Li_2CO_3 mixtures thermally decompose to yield CO and CO_2 at temperatures above 650 °C.[26,27] We therefore propose, that the CO and CO_2 observed in the high temperature region of Figures 1a and 1b are due to the carbothermal decomposition of LiOH and Li_2CO_3 species within the hydrogenated graphite sample. The fact that the *as synthesized-HG* sample reabsorbs H_2O from ambient atmosphere also supports this claim, as LiOH is hygroscopic.

To verify these species were responsible for the high temperature TGA behavior observed for the *as synthesized-HG*, TGA-MS experiments were carried out using 1:1 mass mixtures of $LiOH{\cdot}(H_2O)$: graphite and Li_2CO_3: graphite samples, which are shown in Figure 3. Above 700 °C, both samples demonstrate significant mass loss, comparable to what is observed for the *as synthesized-HG* sample demonstrated in Figures 1a and 1b. This mass loss coincides with the generation of CO and CO_2, however, similar to the *as* *synthesized-HG*, the intensity of the mass spectrometer signal does not completely account for the mass loss observed. With the melting point of Li_2CO_3 at 723 °C, we attribute the remaining mass loss to the volatilization and/or effervescence of Li species, which subsequently condense within the instrument before reaching the MS detector. Residues found within the TGA-MS furnace support this hypothesis. These data demonstrate that Li-contaminates persist in the as-synthesized HG samples and contribute the significant mass losses observed at higher temperatures (> 600 °C).

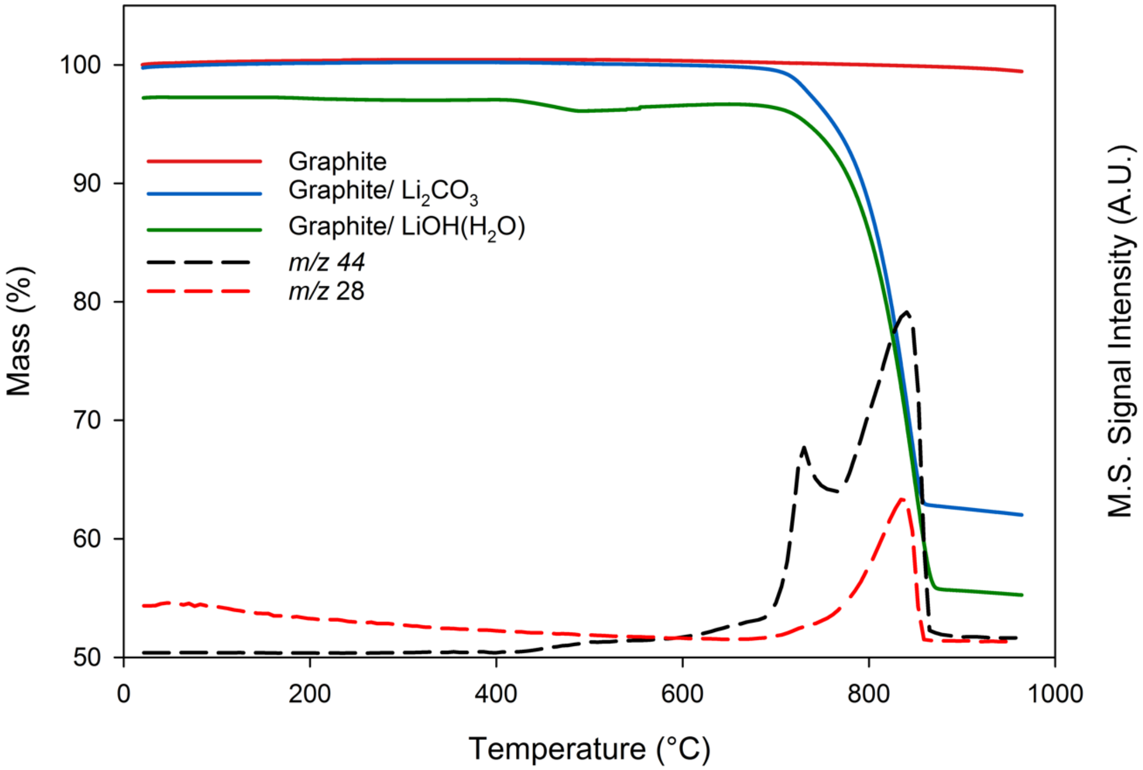

Figure 3. TGA profiles for (red) graphite, (blue) graphite/Li_2CO_3 mixture, and (green) graphite/ LiOH·(H2O) mixture. MS profiles for CO and CO_2 overlapped for the graphite/ LiOH·(H2O) mixture.

4.2 Post-synthetic Purification of Hydrogenated Graphite

4.2.1 Acid Treatment

The results discussed above demonstrate Li-species persist as contaminates in the *as synthesized-HG* sample. In an attempt to purify the sample of Li contaminates, and thus improve the utility of hydrogenated graphite for hydrogen storage applications, the *as synthesized-HG* was treated with acidic solutions under various conditions, and then analyzed by TGA-MS and XRD. The exact details of every “acid treatment” are provided in Section 3 of this manuscript.

In an initial attempt to strip the HG sample of Li-species, the *as synthesized-HG* was finely ground with a mortar and pestle, then suspended in a solution of either 1M or concentrated HCl, and stirred overnight (hereafter referred to as “*1M HCl-HG*” or “*Con. HCl-HG*”, respectively). The following day, the samples were dried via vacuum filtration, and washed with deionized water multiple times, until the pH of the sample solutions were measured to be neutral. The samples were finally dried under vacuum at 350 °C for 1h. Figure 4a shows the TGA profiles for the *1M HCl-HG*, *Conc. HCl-HG* and the original *as synthesized-HG* samples. In comparison to the *as synthesized-HG*, the HCl treated samples exhibit no mass loss at temperatures below 100 °C, and significantly less mass loss at temperatures beyond 600 °C. Furthermore, in comparison to the *1M HCl-HG* sample, the *Con. HCl-HG* sample shows relatively greater mass loss in the region associated with H_2 liberation and less mass loss in the higher temperature region associated with Li contamination. This result demonstrates that the treatment of HG with HCl:

1) Removes impurities from the sample which cause reabsorption of water from the ambient atmosphere,

2) drastically reduces the presence of Li-species that decompose at temperatures > 600 °C, and

3) increases in effectiveness as the concentration of the HCl solution increases.

Given this result, as well as the data presented in the previous section, we postulate that a large fraction of the Li contaminates in the *as synthesized-HG* exist as $LiOH\cdot(H_2O)$, and that treatment with concentrated HCl is sufficient to remove or passivate a large fraction of these species.

Although the *Con. HCl-HG* sample demonstrated a significant reduction in sample mass loss at temperatures above 600 °C, a total mass loss of about 8% is still observed from 600-975 °C. In an attempt to characterize any Li species that may still persist after acid treatment, XRD was again used to characterize the HG samples after heat treatment at 550 °C. Figure 4b shows magnified sections of the XRD patterns for both the *as synthesized-HG* and *Con. HCl-HG* after being heated under vacuum to 550 °C for 1 hour. Surprisingly, reflections corresponding to the crystal structures Li_2CO_3, LiCl and $LiOH\cdot(H_2O)$ are still observed for the *Conc. HCl-HG* sample, suggesting significant Li species still persist, even after treatment in concentrated HCl.

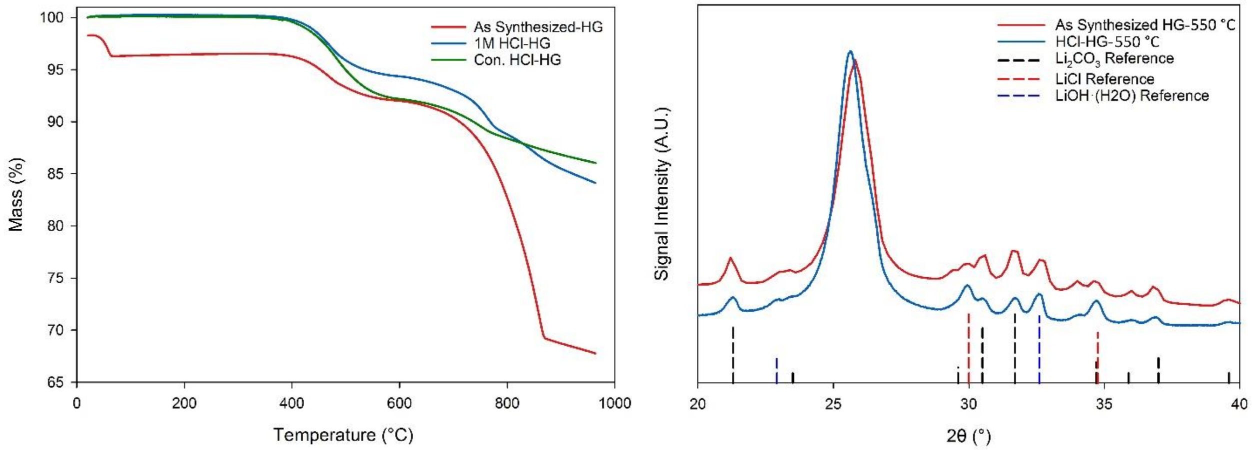

Figure 4. a) TGA profiles for (red) *As Synthesized-HG*, (blue) *1M HCl-HG*, and (green) *Conc. HCl-HG*. b) Magnified XRD patterns for (red) *As Synthesized-HG-550 °C*, and (blue) *HCl-HG-550 °C*. Reference patterns for Li_2CO_3, LiCl, and $LiOH\cdot(H_2O)$ also included.

Since initial treatments using concentrated HCl were not sufficient to entirely remove Li impurities, additional purification strategies were investigated. Different acid solutions, including nitric, sulfuric, phosphoric, and acetic acids were tested, ranging from fully concentrated to 1M, under identical conditions to those described above. Notably, treatment of the as *synthesized-HG* sample with concentrated nitric and sulfuric acid completely stripped the sample of chemically bound hydrogen, as no H_2 gas was detected during TGA-MS analysis.[3] This is most likely due to the strong oxidizing nature of these acids. Besides this result, treatment of the *as synthesized-HG* with other acidic solutions yielded nearly identical results to those described for the HCl treatments. These data are not displayed for the sake of brevity.

4.2.2 Alternative Purification Strategies

With the goal of obtaining an HG sample free of residual Li species, additional attempts were made to purify the *as synthesized-HG*. These included purifying the HG sample via liquid-liquid extractions, sonication of the sample, and heating of the samples under a pressurized atmosphere to “ripen” the Li species before acid digestion. To identify any Li species that may persist after these procedures, the samples were heated to 550 °C under vacuum for 1 hour and then characterized by XRD. The corresponding XRD patterns are provided Figure 5, along with reference patterns corresponding to appropriate Li-containing crystal structures. The rationale for these experiments along with brief procedural details and interpretation of Figure 5 are provided in the subsequent paragraphs, while thorough experimental details of each procedure can be found in Section 3 of this manuscript.

4.2.2.1 Liquid-Liquid Extraction

Like graphite and graphane, hydrogenated graphite is considered hydrophobic.[28,29] Accordingly, previous authors have utilized traditional liquid-liquid extractions to isolate hydrogenated graphite from aqueous suspensions.[7,8,12] Since this work was focused on the large-scale synthesis and application of hydrogenated graphite, liquid-liquid extractions were initially avoided, as the large volume of organic solvent required to extract multi-gram quantities of hydrogenated graphite was considered to be cost prohibitive. However, to be exhaustive, liquid-liquid extractions were investigated as a means of purifying HG of Li contaminates. In two parallel experiments, *as synthesized-HG* was treated in concentrated HCl overnight, then added to a separatory funnel and mixed with an equal volume of either a) hexanes or b) dichloromethane (DCM). After vigorous mixing, the HG sample partitioned to the organic phase, and the aqueous phase was decanted. In each experiment, the sample was washed several times with deionized water, until the aqueous phase was measured to have a pH of 7. Unfortunately, XRD analysis of the liquid-liquid extracted samples demonstrated Li-byproducts still persisted. It should be noted that DCM served as a more effective medium for extrication, as the phase rests at the bottom layer of the separatory funnel, better facilitating HG recovery.

4.2.2.2 Sonication

Given the results discussed to this point, it appears some amount of Li-contaminates robustly persist in the *as synthesized-HG* product. It is therefore plausible to believe these Li species are somehow enveloped, or otherwise physisorbed within the HG matrix. Accordingly, sonication was investigated as a means of stripping these species from the graphite. Briefly, 10 g hydrogenated graphite was suspended to 1.5 L deionized water, stirred, and agitated via a horn sonicator for 1 hour. Over this time, 12 kJ of energy was delivered to the solution via sonication, which was enough to heat the bulk solution to 65 °C. Afterwards, the suspension was immediately added to a separatory funnel and rinsed via liquid-liquid extraction with DCM as described above. As indicated in Figure 5, this sonication experiment proved ineffective at removing residual Li contaminates.

4.2.2.3 Thermal Ripening

Finally, ripening experiments were carried out in an attempt to make the Li contaminates more susceptible to acid digestion. As demonstrated by XRD in Figure 2, the Li species become more crystalline upon heating to 550 °C. We propose this is due to a thermal ripening effect, which promotes the coalescence of Li species into larger and more crystallographically defined structures.[30] We therefore hypothesized similar thermal treatments could be used to promote the coalescence of Li-species into larger, more readily digestible structures. To test this, the as synthesized sample was sealed in a pressure reactor and heated to 350 °C under either a) ambient atmosphere, or b) 300 PSI H_2, and held for 1 hour. After cooling, the samples were treated with concentrated HCl as described in section 4.1. As demonstrated by Figure 5, neither ripening experiment proved effective in removing additional Li impurities.

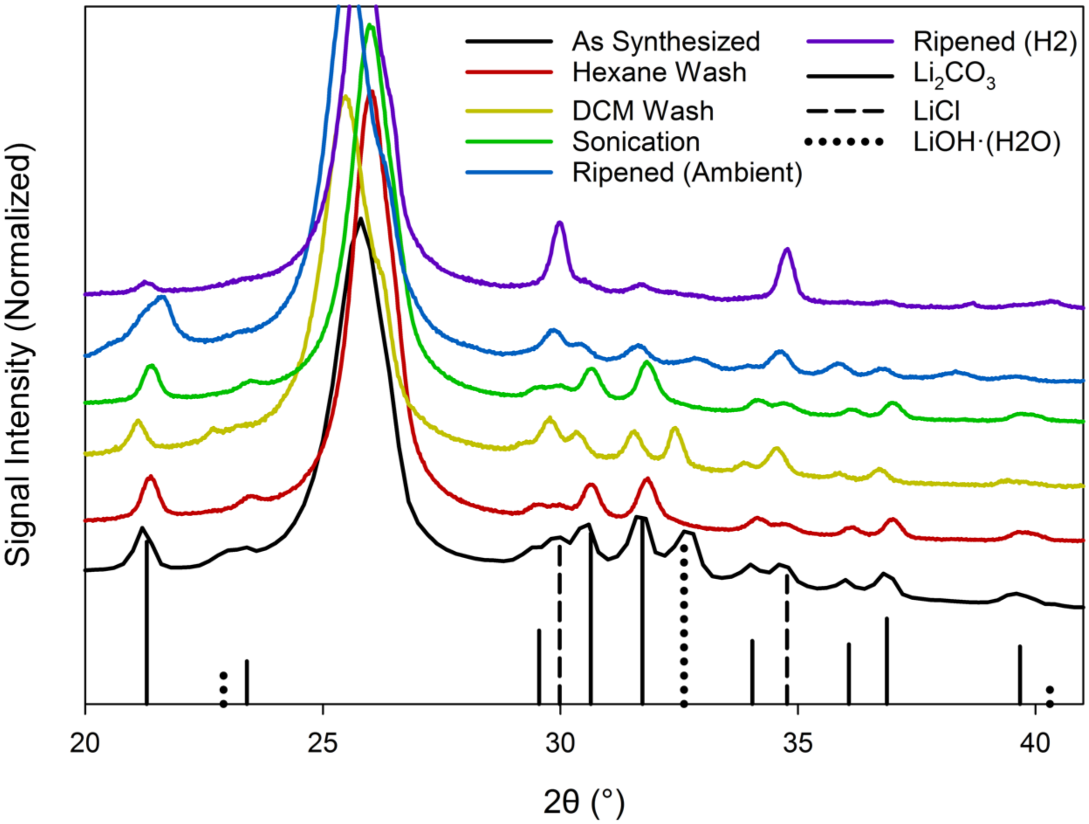

Figure 5. XRD patterns corresponding to the *As Synthesized-HG*, after various purification treatments. All samples were heated to 550 °C under vacuum for 1 hour prior to characterization.

4.2.3 Purification Summary

Significant reduction in unwanted byproducts was accomplished by suspending the hydrogenated graphite sample in an HCl solution. Unfortunately, this was not sufficient to completely remove lithium impurities. Alternative purification strategies were investigated, however, XRD characterization of the treated samples demonstrated residual Li species always persisted in some form. It is notable that different Li species, including LiCl, LiOH·(H2O) and Li_2CO_3 were observed at varying degrees, which appears to depend on the treatment method used.

Such contamination from residual alkali metals in chemically hydrogenated graphite has been acknowledged by some authors[7,13], however, the majority of reports do not include mention of such contamination. The scaling up of the synthesis of hydrogenated graphite may contribute to greater quantities of alkali contamination, but it is also possible alkali contamination has been overlooked in previous reports. The challenges associated with post-synthetically purifying hydrogenated graphite suggests care should be taken to minimize the generation byproducts in the large-scale synthesis of the material (i.e. using optimized reagent ratios, and extreme care following synthetic protocol). Schäfer, et al have noted a reduction in alkali contamination with the use of smaller graphite particles,[8] and this strategy will be investigated along with other optimization parameters moving forward.

4.3 Large-Scale H_2 Liberation

Although TGA-MS characterization is useful for diagnosing temperatures of decomposition, it is insufficient for quantitatively analyzing the gas evolved during sample heating. In order to better characterize the total gases evolved from the thermal decomposition of the hydrogenated graphite, large-scale experiments were carried out using a high pressure reactor (Parr instruments: 4760 HP/HT) connected to a mass spectrometer.

Assuming ideal gas behavior, the quantity of gas generated by heating the hydrogenated graphite sample can be calculated using the ideal gas law relationship:

$$PV = nRT$$

Figure 6a provides a box diagram of the experimental setup used to quantify the gas storage capacity of the hydrogenated graphite. The system consisted of a 0.6 L pressure reactor, which was plumbed to a 3-way junction leading to a vacuum pump and mass spectrometer, respectively. A known quantity of hydrogenated graphite was added to the reactor, which was then held under vacuum and at room temperature for 30 minutes. Next, the valve to the vacuum pump was closed to isolate the pressure reactor, which was then heated to 550 °C and held for an additional 15 minutes to allow the pressure and temperature within the reactor to stabilize. The final pressure was recorded and used to calculate the quantity of gas evolved from the sample. Following the pressure measurement, the valve connecting the reactor to the mass spectrometer was opened, in order to quantify the gas composition.

Using the setup described above, experiments were carried out on three different HG samples: *as synthesized-HG*, acid treated HG isolated via DCM-H_2O liquid-liquid extraction (*DCM-HG*), and acid treated HG rinsed with water (*H_2O-HG*). In order to confirm if 550 °C is sufficient to fully liberate the bound hydrogen, an additional experiment was carried out at 600 °C for the *as synthesized-HG*. Table 1 provides values corresponding to the loading capacities and gas compositions for the corresponding samples after heating to 550 °C and 600°C, respectively. The hydrogen released during these experiments corresponds to between 3.15 to 4.26 wt.% (40.7 to 55.1 % of the theoretical H_2 loading capacity predicted for a fully hydrogenated sample). Comparing the *DCM-HG* and *H_2O-HG* to the *as synthesized-HG* sample samples shows an approximate 33% increase in H_2 loading capacity, for both samples, demonstrating post synthetic treatment can significantly improve H_2 storage capacity. There appears to be no significant differences between the product gases generated from the *DCM-HG* and *H_2O-HG* samples. With respect to the two acid treated samples, the relative composition of the evolved gases shifts to a greater fraction of H_2, as lesser fractions of CH_4, NH_3 and H_2O are observed relative to the *as synthesized-HG* sample. Additionally, no significant difference in H_2 loading was observed when the *H_2O-HG* was heated to 600 °C, suggesting 550 °C is sufficient to liberate the vast majority of hydrogen under these conditions. It is also worth noting, no detectable amount of CO or CO_2 was observed in these experiments, although trace amounts of these species were observed in this temperature for the TGA-MS experiments described by Figures 1a and 1b. Following this result, we believe the CO_2 signal below 550 °C in Figures 1a and 1b is due to contaminants within the TGA furnace.

Table 1. Hydrogen loading and gas composition corresponding to the large-scale decomposition of HG samples.

550 °C							
Hydrogenated Graphite Sample	**H_2 Loading Capacity (wt.%)**	**Theoretical H_2 Loading (%)**	**H_2 (%)**	**CH_4 (%)**	**NH_3 (%)**	**H_2O (%)**	**N_2 (%)**
As Synthesized-HG	3.15	40.7	88.2	5.4	3.2	0.9	2.3
DCM Wash	4.17	53.9	91.5	4.1	1.5	1.2	1.7
H_2O Wash	4.22	54.5	92.0	4.0	1.4	1.1	1.5
600 °C							
Hydrogenated Graphite Sample	**H_2 Loading Capacity (wt.%)**	**Theoretical H_2 Loading (%)**	**H_2 (%)**	**CH_4 (%)**	**NH_3 (%)**	**H_2O (%)**	**N_2 (%)**
H_2O Wash	4.26	55.1	89.4	4.3	1.7	1.4	3.2

The TGA-MS data presented in Figure 1 suggests that treating the hydrogenated graphite at elevated temperatures may reduce the presence of contaminating species. To test if this strategy could be employed to improve HG purity, the large-scale experiments described in Table 1 were repeated, but with the samples held under vacuum at 325 °C (instead of room temperature) for 30 minutes before the reactor was isolated and heated further. Table 2 provides values corresponding to the loading capacities and gas compositions measured for the same samples after vacuum treatment at 325 °C. Surprisingly, the percent composition of the liberated gas corresponding to H_2 is nearly identical to the values observed in Table 1, suggesting vacuum treatments at elevated temperatures do not significantly improve the purity of the hydrogenated graphite. Furthermore, the vacuum treatments at elevated temperatures appear to reduce the amount of captured H_2, leading to lower calculated H_2 loading capacities, on the order of roughly 20% less than what was observed for the values reported in Table 1.

The lower H_2 loading capacities demonstrated in Table 2 indicates vacuum treatment at 325 °C reduces the overall storage capacity of the hydrogenated graphite, and suggests the material should not be substantially heated under vacuum before it is applied for hydrogen storage applications. Initially, this result appears contrary to the TGA-MS results in Figure 1, which indicated heated vacuum treatments would improve the purity and hydrogen loading of the hydrogenated graphite sample. This hypothesis however, assumes such vacuum treatments do not significantly facilitate the dissociation of H_2 from the hydrogenated graphite. Interpretation of Tables 1 and 2, however, suggest vacuum treatments at 325 °C do indeed promote a noticeable loss in H_2 yield.

Table 2. Hydrogen loading and gas composition corresponding to the large-scale decomposition of HG samples after 325 °C vacuum treatment.

550 °C							
Hydrogenated Graphite Sample	**H_2 Loading Capacity (wt.%)**	**Theoretical H_2 Loading (%)**	**H_2 (%)**	**CH_4 (%)**	**NH_3 (%)**	**H_2O (%)**	**N_2 (%)**
As Synthesized-HG	2.71	35.0	87.0	8.0	3.5	1.1	0.4
DCM Wash	3.14	40.6	92.0	4.2	2.1	0.5	1.2
H_2O Wash	3.18	41.1	91.6	4.3	2.3	0.6	1.2

Because fuel cell performance and lifetime are influenced by the purity of the feed gas, any gas evolved from hydrogenated graphite should be purified before fuel cell operation. To demonstrate the gas evolved from hydrogenated graphite could be easily purified, a packed carbon filter (Supelco -PN 22445-U) was added to the Parr reactor setup, as demonstrated in Figure 6b. With this new setup, the same experiments outlined in Table 1 were repeated at 550 °C. After passing through the carbon filter, the corresponding gas was found to consist of > 99% H_2 for all tested samples.

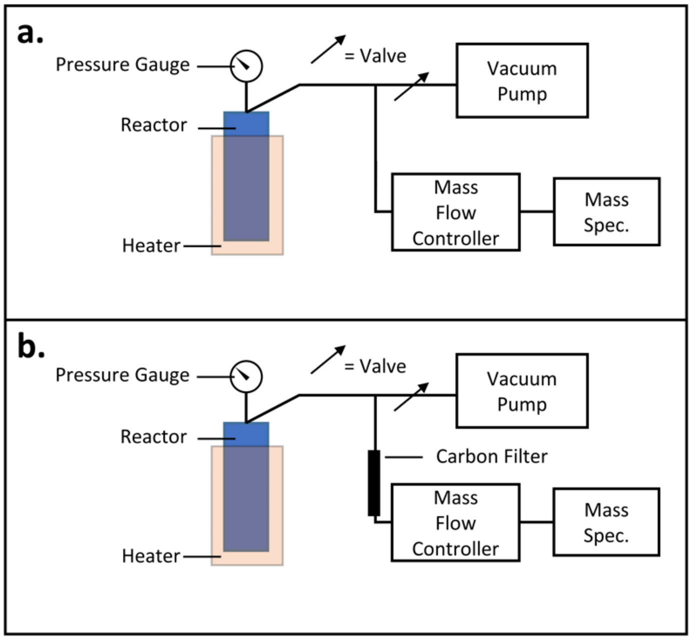

Figure 6. Box diagram of pressure reactor setup a) without, and b) with carbon filter.

5.0 CONCLUSIONS

Hydrogenated graphite provides a means of solid-state H_2 storage with relevant applications for UUV's and other underwater systems. To evaluate the merits of this material for solid-state hydrogen storage, 75 g of hydrogenated graphite was synthesized and then evaluated using a suite of characterization and purification techniques. As synthesized, the hydrogenated graphite sample was found to generate a minority of gases other than H_2 during thermal decomposition which included H_2O, NH_3, CH_4, CO_2 and CO.

TGA-MS experiments provided insights into the temperature range at which these gases evolve from the hydrogenated graphite, and will be useful for developing standard operating procedures for the material moving forward.

Suspending the hydrogenated graphite in concentrated hydrochloric acid was demonstrated to improve the hydrogen storage capacity of the material as well as reduce the generation of unwanted gases during thermal decomposition. The efficacy of acid treatment was found to depend on the concentration of the acidic solution, with higher concentration solutions yielding samples with improved hydrogen storage capacity. Oxidizing acids such as nitric and sulfuric were found to strip the material of chemically bound hydrogen. XRD characterization of the hydrogenated graphite revealed residual lithium species persisted in the material even after treatment with concentrated hydrochloric acid. Accordingly, alternative purification strategies were evaluated, including liquid-liquid extractions, exfoliation via sonication, and thermally induced ripening of the Li contaminates. However, no alternative purification strategies were found to improve the purity of the sample beyond the original acid suspension technique.

In order to evaluate quantity and purity of gas generated from the thermal decomposition of a bulk sample, large-scale experiments were carried out using a high pressure reactor loaded with multiple grams of hydrogenated graphite. Depending on the purity of the sample, the bulk hydrogenated graphite was measured to have a hydrogen storage capacity between 3.15 to 4.26 wt.%. These values correspond to over one half of the theoretical hydrogen storage capacity for fully hydrogenated graphite, suggesting improvements can be made to the current bulk synthetic protocol. Regardless, these current results successfully demonstrate hydrogenated graphite can provide large-scale, solid-state hydrogen storage with a loading capacity approaching the 4.5 wt.% goal set by DOE. Additionally, we demonstrated that the product gas generated from these experiments can be easily purified to > 99% H_2 using a simple packed carbon filter.

6.0 RECOMMENDATIONS

Using the results outlined in this manuscript, we offer the following insights and recommendations in regards to applying hydrogenated graphite as a means of H_2 storage:

1. The synthetic protocol used to chemically hydrogenate multi-gram quantities of graphite was found to generate a product with a hydrogen storage capacity of up to 4.26 wt. %, over one half of the theoretical value for graphane. In order to maximize the H_2 storage capacity of the bulk material, studies aimed at optimizing the large-scale synthesis of hydrogenated graphite are recommended, and are currently ongoing.

2. During heating, a fraction of the hydrogenated graphite's mass is lost before H_2 is generated. Thermally pretreating the hydrogenated graphite to 350 °C under vacuum was therefore believed to be an effective means of improving the material's purity. However, large-scale experiments demonstrate such pretreatment can reduce the overall H_2 loading, by causing desorption of low-temperature bound hydrogen.

3. TGA-MS experiments demonstrate little to no H_2 is generated after hydrogenated graphite is heated above 600 °C, however, byproduct gases such as CO and CO_2 can evolve due to the

presence of residual alkali contaminates. Accordingly, prototype systems operating with a hydrogenated graphite power source should maintain an operating temperature < 600 °C.

4. Suspending the hydrogenated graphite in an acidic solution after synthesis appears to reduce, but not totally eliminate unwanted byproducts and contaminates. Accordingly, a prolonged "acid washing" step should be applied to chemically hydrogenated graphite before it is utilized as a means of H_2 storage. Concentrated HCl is recommended.

5. Although attempts at improving synthetic and purification protocols should be made to minimize the evolution of unwanted gases from hydrogenated graphite, non-trivial quantities of impurities will most likely always persist in any realized product. Accordingly, steps should be taken to purify the product gas stream before it is fed to a fuel cell. As a proof of concept, commercially available carbon filters proved effective at purifying the product gas from hydrogenated graphite, however, more rigorous evaluation of feed gas purification methods should be evaluated in the design of future prototype systems.

7.0 ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research.

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