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An International Laboratory Comparison Study of Volumetric and Gravimetric Hydrogen Adsorption Measurements

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Abstract: In order to determine a material's hydrogen storage potential, capacity measurements must be robust, reproducible and accurate. Commonly, research reports focus on the gravimetric capacity, and often times the volumetric capacity is not reported. Determining volumetric capacities is not as straight-forward, especially for amorphous materials. This is the first study to compare measurement reproducibility across laboratories for excess and total volumetric hydrogen sorption capacities based on the packing volume. The use of consistent measurement protocols, common analysis, and figure of merits for reporting data in this study, enable the comparison of the results for two different materials. Importantly, the results show good agreement for excess gravimetric capacities amongst the laboratories. Irreproducibility for excess and total volumetric capacities is attributed to real differences in the measured packing volume of the material.

Introduction

The transition from the reliance on fossil fuels to the realization of hydrogen fuel for vehicles will require new advances in energy storage. Lightweight, compact, and affordable hydrogen storage solutions that allow for a 300-500 mile driving range without sacrificing vehicle performance or cargo space are needed. The U.S. Department of Energy (DOE) has set forth system targets for on-board hydrogen storage for light-duty vehicles that can reversibly store 4.5 weight percent hydrogen and 0.030 kg hydrogen/liter by 2020.^[1] These system storage targets originated from analysis of driving range, packaging, cost, safety, and performance requirements for the full span of light-duty vehicles, in order to be competitive with the current technology.^[2] This goal has created an active area of material science research that requires not only the development of novel materials, but the

ability to verify hydrogen storage properties accurately and precisely. In the late 1990s and early 2000s, there were a number of notable publications reporting excess gravimetric hydrogen storage capacities that were controversial and brought skepticism to the hydrogen storage field. Many of these results lacked reproducibility for several reasons including gross systematic measurement errors to material inconsistencies. Also, in 2009, the results from a round-robin measurement comparison study by Zlotea *et al.* reported a large degree of irreproducibility of hydrogen excess gravimetric capacity measurements amongst 14 laboratories.^[3] The study compared hydrogen adsorption measurements of a carbon sample at both ambient temperature and 77 K. This eye-opening study highlighted the discrepancies that can occur for hydrogen sorption measurements and signaled the need to understand the origins of the discrepancies, but more importantly, to improve the robustness of such measurements. A recent perspective publication by Broom and Hirscher in 2016 has highlighted the irreproducibility of these past reports.^[4]

Hydrogen storage materials include adsorbents, metal hydrides, and materials with chemically stored hydrogen. Hydrogen sorption capacities of materials can be determined through temperature programmed desorption (TPD), manometric, and gravimetric measurements. Each of these techniques requires careful measurements and calibration. The most commonly used approach is the manometric, or also-called Sieverts method, but the gravimetric technique is used frequently as well. Accurate reporting of sorbent capacity measurements has proven to be elusive in the past. Recently, the hydrogen storage community has progressed with important and impactful recommendations for improving measurement accuracy and analysis, e.g. defined hydrogen storage capacities, volumes,

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The full cycle of adsorption and desorption data at ambient and liquid nitrogen temperatures were requested. The *ambient* temperature was not a specific temperature in order to avoid participants from deviating from their typical instrumental set up. For example, NREL has the reference volume for its manometric instrument set at 303 K and this temperature control can easily be extended to the sample volume as well, which defines NREL's "ambient" temperature measurement. This has the added advantage of making the manometric instrument isothermal and simplifies the resultant mole-balance model, headspace calibration, and data analysis and therefore less prone to experimental error. We expect that the difference in capacities between 303 and 298 K for carbon sorbent samples will not vary strongly in this regime; however, it is possible a couple of degrees may slightly influence the deviations in the data among the laboratories. Similarly, the precise temperature for a liquid nitrogen bath also changes according to geographic altitude of the laboratory and may likewise slightly influence the deviations in the data among the laboratories. Thus, it is for these reasons that we refer to the measurements as ambient and liquid nitrogen temperatures.

A "run sheet" (Figure S1) was provided to each participating laboratory with instructions to complete and return the run sheet with explicit experimental details for each adsorption measurement. The reported data were to include specific experimental measurements, as well as calculated capacities. Guidelines were provided that described the calculation of three different capacities: the excess gravimetric, excess volumetric, and the total volumetric. All storage capacities were to be based on the mass of the sample measured after degassing and hydrogen sorption measurements were completed.

The excess gravimetric capacity in weight percent, $wt\%$, is defined as:

$$wt\% = \frac{100m_{exH}}{m_s + m_{exH}} \quad (1)$$

where m_{exH} is the mass of the Gibbsian excess hydrogen adsorbed and m_s is the mass of the degassed sample. Excess volumetric capacity in g-H₂/L is defined as:

$$\Lambda_{ep} = \frac{m_{exH}}{V_{pk}} \quad (2)$$

where V_{pk} is the packing volume. The packing volume is defined as the volume of the material including the free gas inside the pores of the material and the void spaces in between particles. The total volumetric capacity in g-H₂/L is defined as:

$$\Lambda_{tp} = \frac{m_{totH}}{V_{pk}} \quad (3)$$

where m_{totH} is the mass of the total amount of hydrogen, free and adsorbed, in the packing volume. On a molar basis, the total capacity is:

$$n_{tot} = n_{ex} + \rho_{fg} (V_{pk} - V_{sk}) \quad (4)$$

Here, n_{tot} is the total capacity (moles), n_{ex} is the Gibbsian excess moles of H₂, ρ_{fg} is the molar density of the free gas at the given temperature and pressure, V_{pk} is the packing volume and V_{sk} is the sample's skeletal volume. The skeletal volume is comprised of the volume that the adsorbate molecules cannot permeate or access. For a more detailed discussion of these definitions and the issues concerning them, see Gross, et al.^[5] and Parilla et al.^[6]

The ILC18 did not suggest a method for measuring the skeletal volume of the powders, as each laboratory has their own established method. Typically, He pycnometry or

expansion is used to measure the skeletal volume. Assuming that helium does not adsorb on the sample, measuring the helium pressure for the same volume with and without the sample, or measuring the helium pressure expanded into a known volume containing the sample is used to determine the skeletal volume.

There are numerous standards for determining the packing density of powders, and these are generally focused on very specific materials and their intended use, and so their application to hydrogen storage materials is limited. We did not dictate a standardized method for measuring the packing volume, however the ILC18 protocol stated that the goal was to measure the packing density in the same condition of the material that was used during the hydrogen sorption measurement. For example, if the material was tapped to promote settling in the capacity-measurement sample container, then this should be repeated for the packing-density measurements as well. It was explicitly requested that the participants avoid compressing the samples significantly from their provided state, i.e., no use of a hydraulic or mechanical press to compact the material, as this may cause (micro)structural changes in the material.

The packing density is determined according to equation 5, where the mass (measured after degassing and gas sorption measurements) as well as the volume of the sample must be determined experimentally. For accurate density determination, it is important that the calibrated volume dimensions are large compared to the sample particle dimensions.

$$\rho_{pk} = m_s / V_{pk} \quad (5)$$

Results

The majority of the capacity data was obtained through manometric instrumentation, and only one laboratory reported results using the gravimetric methodology. As previously stated, the data is anonymous and identified using a code number; we have associated each laboratory with this designated number and kept that number consistent for all data from that laboratory.

The experimental parameters and details are listed in Table 1 (Sample 1) and Table 2 (Sample 2). Not all of the laboratories had the capability to measure adsorption at liquid nitrogen temperature. Although not listed in Tables 1 and 2, all measurements were performed using hydrogen gas with a nominal purity of 99.999% or greater. It was also noted that all participants measured hydrogen sorption after degassing the sample without exposing the sample to air.

For this study, determining the skeletal and packing volumes (which also determines the corresponding densities) are essential since they are needed to calculate the requested capacities. This is especially true for the packing volume due to the definitions of the volumetric capacities. It is possible to avoid determining the skeletal volume (density) by directly measuring the headspace calibration or sample buoyancy correction using helium for ambient-temperature measurements. However, some instruments do not have this option and therefore would require an independent determination of the skeletal volume. It is not recommended to perform a direct calibration with helium at low temperatures, so when making those measurements, the skeletal density is needed to allow proper calibration.

Twelve laboratories used helium to measure the skeletal volume of the samples, and one lab assumed a skeletal density. Figure 2 shows the comparison of the measured skeletal density for Sample 1 a) and Sample 2 b). The median of reported values is shown as a solid line, and the mean of the values is shown as

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a dash/dot line. The two dotted lines show the higher and lower threshold limits for outliers. Both the packing and skeletal densities' raw data were analyzed for possible outliers. (The complete description of this procedure is described in the supplementary information). It is interesting to note that Sample 1 skeletal density had only one outlier while Sample 2 had three outliers where the thresholds fall about $\pm 15\%$ of the mean. The amount of scatter is slightly greater for Sample 2 (relative standard deviation (RSD) = 6.1%) than Sample 1 (RSD = 5.1%). This was not unexpected since the powder sample (Sample 2) is more difficult to handle which may have made accurate mass measurements more difficult. If the outliers were included in the statistics, then both RSDs would have increased substantially with Sample 1 RSD = 11.6% and sample 2 RSD = 18.3%.

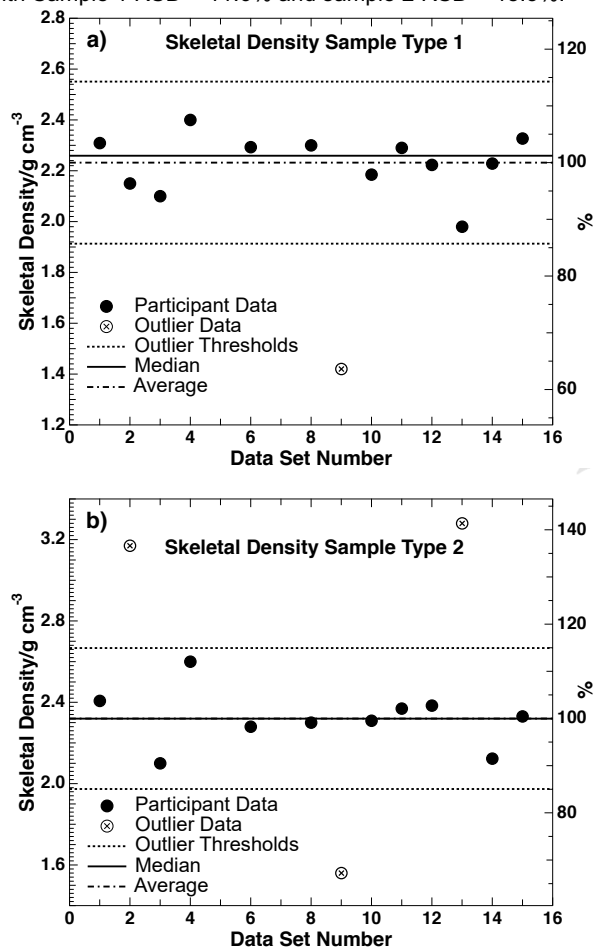


Figure 2. Measured skeletal densities for a) Sample 1 and b) Sample 2.

The participants reported measuring the packing volume using different methods. One laboratory measured the volume using a glass rod with the same diameter as the sample holder, another reported determining the volume based on the "container size". Four laboratories tapped the material in a graduated cylinder, while one lab did not tap but also used a graduated cylinder. Three participants tapped the material ~ 10 times and measured the volume based on the mass of water displaced in the sample volume. One laboratory used a "pressed and tapped syringe method" that involved pouring 1 mL of material into a capped 1 mL syringe that was then tapped 120 times with ~ 2 cm strokes on a hard lab table. Individual particles cracked under the "pressed and tapped syringe method" that proved more applicable for Sample 2. One laboratory did not report their

method for measuring the packing volume. Finally, one laboratory did not report volumetric data and therefore did not measure the packing volume.

The reported packing densities for Sample 1 and 2 are shown in Figure 3 a) and b) respectively using the same demarcation for median, mean and outliers and the right and left axes. Note that the right axes have drastically different scales which show the increased variation in the measured packing density of Sample 2 compared to Sample 1. For each data set, there is one outlier, each from the same laboratory. This likely indicates a flawed methodology for measuring the packing density or perhaps miscommunication of what was being asked for. What is striking is that the RSDs are markedly different for the two samples. Sample 1 has a RSD of 4.6%, while Sample 2 has a RSD of 27.8%, over 6 times larger. This is also reflected in the outlier analysis in that the outlier thresholds were again about $\pm 15\%$ of the mean for Sample 1 packing density, but for Sample 2, they are approximately $\pm 80\%$. One laboratory noted that the packing volume of Sample 2 actually increased by 21% by moderate tapping <100 times, contrary to common expectations.

The variations in the measurement methodology, sample preparation, and the nature of the sample itself undoubtedly contributed to increased variation of the measured sample density. It should also be explicitly stated that this variation does not necessarily correspond to measurement error per se, but rather indicates the sensitivity of the measured results on the protocols used to obtain those results.

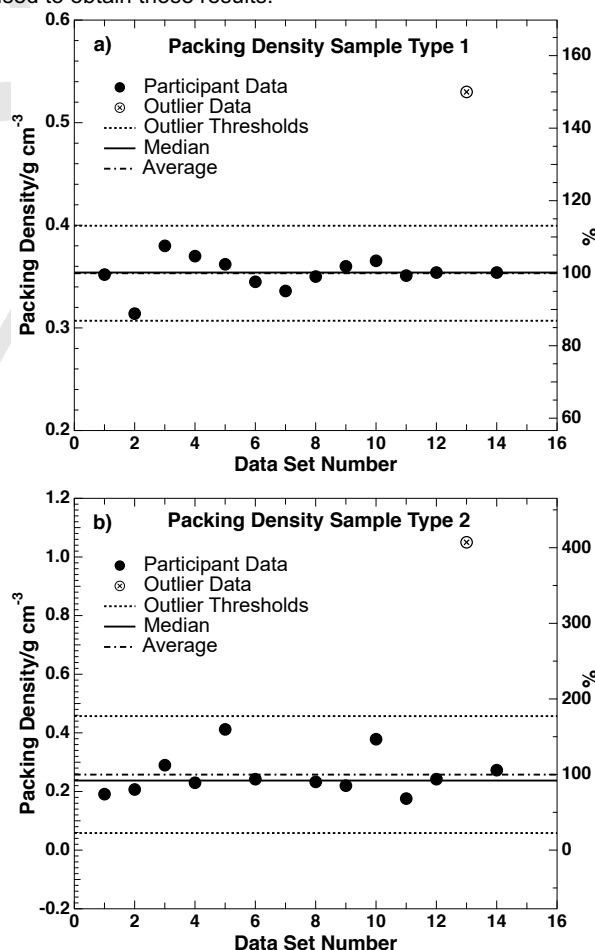


Figure 3. Packing density for a) Sample 1, and b) Sample 2

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Outlier Analysis for Densities

With regard to the measured values of the skeletal and packing densities, there were some values that were significantly different than the majority of the values. It therefore raises the question if these particular values should be considered as outliers and not included in the main analysis of densities. To address this question, we applied accepted outlier statistical tests to these data using the generalized Extreme Studentized Deviate (ESD) protocol.^[24, 25] Details of the outlier tests are given in the supplementary text. The tests identified 1 outlier each in the packing density for sample types 1 and 2, and the skeletal density for sample type 1; and it identified 3 outliers for the skeletal densities for Sample 2.

Given that outliers have been identified for the skeletal and packing densities, we then explored whether these outlier values dominate the resulting isotherm capacity determinations. The influence of the skeletal density on the excess gravimetric capacity depends on the cell calibration methodology. It is possible to calibrate the cell volume directly with the sample inside the cell at ambient temperature. In this case, (case A) the skeletal density is not needed for determining the gravimetric excess and perhaps was independent of the skeletal density determination. Alternatively, (case B), the skeletal volume can be subtracted from the empty cell calibrated volume and used to calculate gravimetric excess. ILC18 did not ask participants which model was used. We chose not to eliminate any of the isotherm data sets from the statistical analysis even if the skeletal density was designated as an outlier for the associated isotherm data set. The justification for this stems from the type of error that this would introduce: it is equivalent to an error in the headspace calculation. The impact of general headspace error can be lessened by using adequate sample mass (more so in case A than B). For all skeletal density outliers, each of the labs used at least 300 mg of sample, which helps to minimize non-skeletal-density contributions to the headspace error.

This was not the case for the outliers in packing density where by the very definitions of the volumetric capacities (see Eqns. 2, 3, & 4), the calculations depend directly on the packing volume. Participant 13 had outlier packing densities for both Sample 1 and 2; therefore, the data for the excess volumetric and total volumetric capacities are removed from the analyzed data (i.e., the excess and total volumetric capacities are not included in the statistics of these capacities). The packing volume is not a factor in calculating the excess gravimetric capacity, therefore the data from Participant 13 is included in that set of analyzed data.

Adsorption Capacities

We have separated the discussion of the data by the three different capacities: excess gravimetric, excess volumetric and total volumetric. First the data as-reported from the participants is shown. This includes data, in some cases, where participants self-reported errors associated with the measurement. This data is shown in grey and was not included in the statistical analysis. When appropriate, gross errors were corrected by the participant. The data reported by each participant includes one cycle, defined as adsorption and desorption. Three participants only reported the adsorption portion of the cycle. In order to be able to compare the pressure-composition-temperature (PCT) data statistically, it is necessary to do so at a set of common pressures for all the isotherms. This was accomplished by choosing a set of common pressures and then interpolating the different isotherm data sets to those pressures. A linear interpolation algorithm between each pair of actual data points was chosen to provide those values as it was straightforward to implement and guaranteed that all the actual data points would be captured. No extrapolation was

performed outside the minimum or maximum of the actual pressures that were measured. For this analysis, only adsorption data was considered. A list of all the interpolated points is given in Tables S1 - S12, and shown in Figures S2-S7 in the supplementary material. Note that the values listed in these tables show 3 significant digits in order to display in table format. All statistics as well as the RSD are calculated based on the interpolated data without limiting the number of significant digits.

Excess Gravimetric Capacity

Calculating the gravimetric capacity is the most straightforward of the three capacities. It is calculated by dividing the mass of adsorbed gas by the sample weight and the mass of the hydrogen as shown in Equation 1. The as-received ambient temperature hydrogen adsorption and desorption data for Sample 1 and Sample 2 are shown in Figure 4 a) and b). The difference in "ambient temperature" amongst the collected data is 6 K. Figure 4 a) includes 14 data sets using manometric instrumentation and 1 data set using gravimetric instrumentation, and Figure 4 b) shows 13 data sets using manometric instrumentation and 1 data set measured with gravimetric instrumentation.

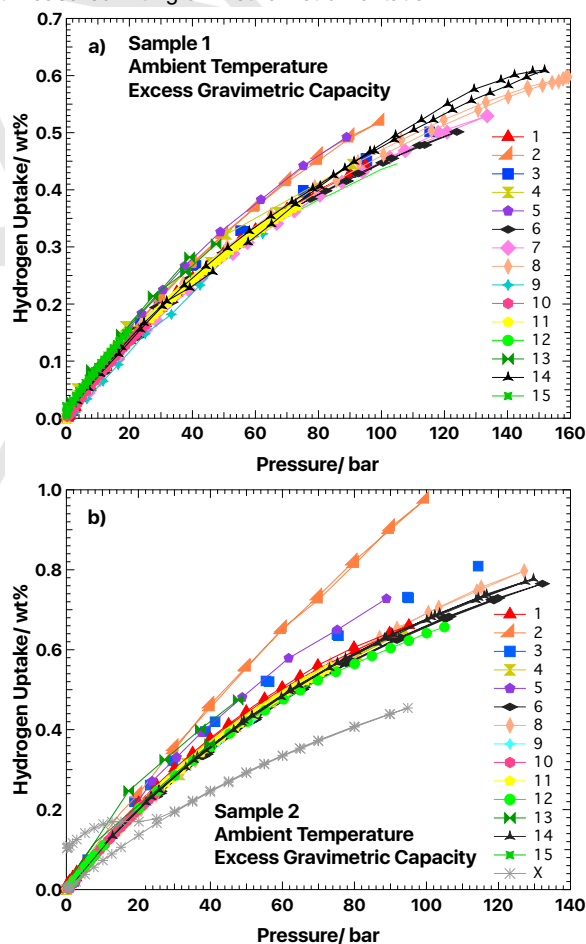


Figure 4. As-reported excess gravimetric capacities at ambient temperatures for a) Sample 1, and b) Sample 2.

The majority of the excess gravimetric capacities for Sample 1 lie in a pack at low pressures until 45 bar. At pressures greater than 45 bar, the excess gravimetric data from two participants show somewhat higher capacities. The sample size of these two measurements was 0.6328 g and 0.800 g, which are in the middle of the distribution of sample sizes measured. The gravimetric

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excess capacities for Sample 2 at ambient temperature show relatively good agreement up to 30 bar, at which point, three data sets diverge from the pack of results from the other 9 laboratories. The most divergent data has the third lowest sample mass of 0.3099 g, and the data appears to be more of a linear slope with pressure.

The grey data in Figure 4 b), labelled as "X" represents a data set with an experimental error reported by a participant. It is shown here for discussion and not included in analysis of the results in Figure S2 b). The participant reported that upon completion of the experiment, the sample had been partially evacuated from the sample cell and migrated to the rest of the instrument. The effect of the system contamination is evident in the shape of the desorption portion of the curve at pressures below ~25 bar, where the data no longer represents reversible physisorption. This is the point in the experiment in which the sample likely transferred outside of the sample cell. While normalization of the data by a larger mass would decrease the calculated amount of adsorption, the error associated with sample migration on the moles-adsorbed calculation are complicated and not straightforward. However, from the shape of the curve, it is evident that this data set is questionable.

This prompted us to recommend to the other participants in the study to use a 2 μm particle filter in order to avoid powder leaving the sample cell. Unfortunately, this resulted in the participant having to thoroughly clean their instrument of the sample powder in the instrument reference volume. The laboratory decontaminated their system, and re-measured adsorption of a new aliquot of Sample 2 for which their data lies in the middle of the pack in Figure 4 b).

Statistical analysis of the interpolated adsorption data from each data set (Figures S2 a) and b)) reveal the variation of the gravimetric excess capacity of Sample 1 at ambient temperature is much smaller at lower pressures and increases with increasing pressure. This effect is expected and noted by previous studies comparing the reproducibility of adsorption isotherms.^[3]

The as-reported data measured at liquid nitrogen temperature for excess gravimetric capacity are shown in Figure 5 a) and b). There is a 2 K difference in temperature for liquid nitrogen temperature due to ambient atmospheric pressure and the altitude of the participating laboratories. Fewer participating laboratories had the capability to measure adsorption at liquid nitrogen temperature than at ambient temperature. The data in Fig 5 a) (Sample 1) includes 9 measurements using the manometric technique and 1 measurement using the gravimetric technique, and Fig 5 b) shows 8 measurements using the manometric technique and 1 measurement by the gravimetric technique, (Sample 2).

The grey data in Figure 5 a) was reported as an experimental error, for which the participant did not properly calibrate the headspace volume. In this case, the researcher did not maintain the same experimental sample tube configuration for the calibration of an empty holder as the configuration used when filled with sample for the hydrogen adsorption measurement. The effect of this error is small at lower pressures; however, an improper calibration of the sample holder has a larger effect at higher pressures and this is expected for headspace errors. This data is only shown here for discussion and not included in the analysis shown in Figure S3.

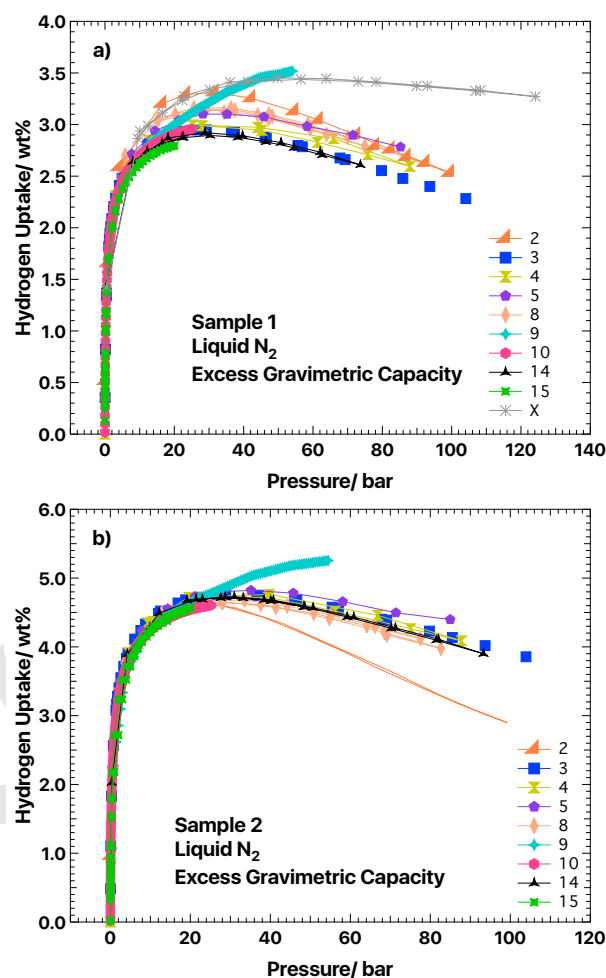


Figure 5. As-reported gravimetric excess capacities at liquid N_2 temperature for a) Sample 1, and b) Sample 2.

The overall variation in the excess gravimetric capacities in (Figure S3) below 22 bar is quite low; Sample 2 has a tighter distribution than Sample 1. The variation for both samples increases after the isotherm folds over at higher pressures. This folding over of the isotherm is a consequence that only Gibbsian excess adsorption can be measured and as the free-gas density approaches the adsorption density, it will effectively subtract from the measured result. The isotherms for Participant 9 data in Figure 5 a) and b) do not fold over at ~22 bar, which is unexpected. The cause for the deviation of the data from Participant 9 is currently undetermined. The unusual isotherm shape for both samples suggest a systematic error, but of unknown origin. The Sample 2 excess gravimetric capacity reported from Participant 2 is lower than that from other labs for pressures greater than 30 bar; the cause of this is also not known, but it has the characteristics of a headspace calibration error.

Excess Volumetric Capacity

The as-reported excess volumetric capacities, as defined in equation 2, measured at ambient temperature are shown in Figure 6 a) and b) for Sample 1 and Sample 2, respectively. All data in these graphs are based on manometric measurement techniques. In both graphs, the data for participant 13 is greyed out due to this laboratory's outlier value reported for packing density for both Sample 1 and Sample 2, shown in Figure 3. We

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have not included this data set for the analysis of the data as shown in Figure S4 a) and b).

In general, there is a greater variation in the reported excess volumetric capacities for both Sample 1 and Sample 2 than in the reported excess gravimetric capacities. Additionally, the statistical analysis shown in Figure S4 a) and b) shows that the variation is much larger for Sample 2 than Sample 1. This variation in excess volumetric capacity reflects, and can be attributed to, the different measured packing densities and their variation. It is important to keep in mind, that there are no accepted packing densities for these materials and they depend strongly on how the packing density was measured and how the sample was processed for that measurement. Figure 6 represents a natural spread due to these packing-volume variations and correlates with the previous variations seen in the gravimetric excess capacities (Figure 4). It does not suggest that the measurements from one laboratory are more correct than another laboratory, as the differences in the packing density measurements are real. These data show that variations in volumetric capacity determinations based on the packing volume of nominally identical materials are largely attributed to the variations in those packing volumes.

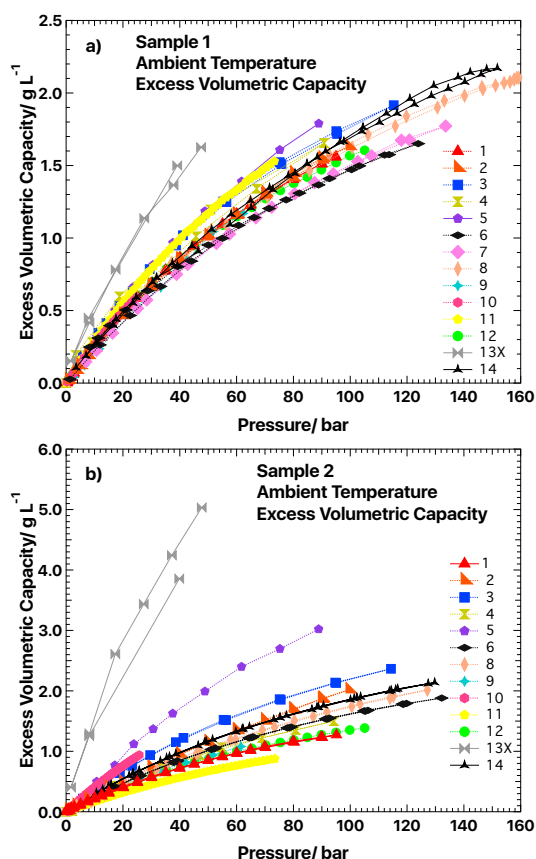


Figure 6. As-reported excess volumetric capacities at ambient temperature for a) Sample 1, and b) Sample 2.

The as-reported excess volumetric capacities, at liquid nitrogen temperatures are shown in Figure 7 a) and b). The range of excess capacities is greater for Sample 2 than Sample 1, due to the greater variation in the packing volumes of Sample 2. This is readily apparent when we directly compare the gravimetric data with the excess volumetric data. This is observed by the expanded box sizes in Figures S5 a) compared to Figure S3 a) due to the modest ~5% additional variation that Sample 1's

packing density contributes to that capacity variation. Comparing the variation in data for Figures S3 b) to S5 b) shows an increase which reflects the substantial differences in Sample 2's packing density.

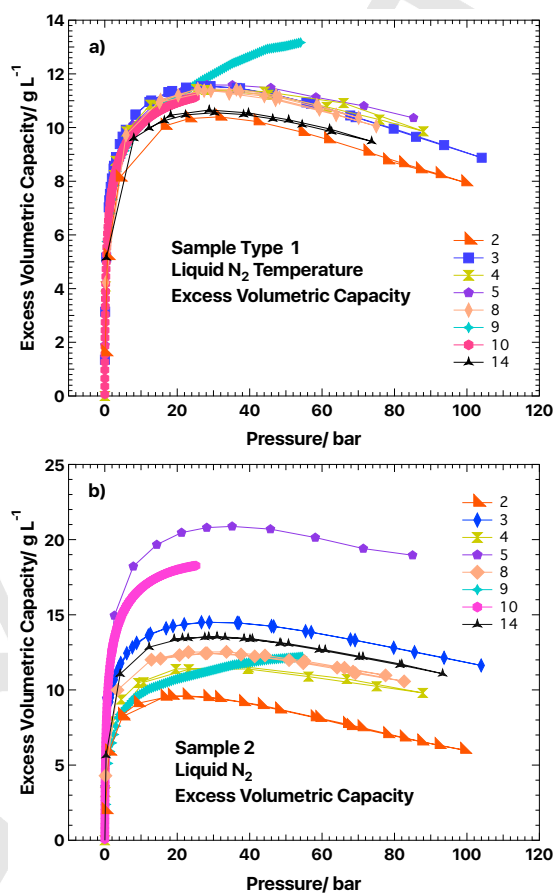
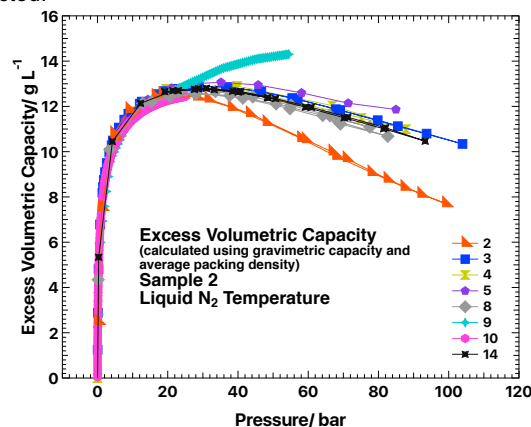


Figure 7. As-reported excess volumetric capacities at liquid N₂ temperatures for a) Sample 1, and b) Sample 2.

This point is further illustrated by recalculating the excess volumetric capacity from the excess gravimetric capacity, but using a single common value for the packing density, in this case, the mean of Sample 2's packing density. This result is shown in Figure 8 and the graph with its intrinsic variations closely mimics the variation of the gravimetric excess (Figure 5 b) as is to be expected.



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Figure 8. Excess volumetric capacities of Sample 2 at liquid nitrogen, calculated using the reported gravimetric data and using the study's average packing density.

Total Volumetric Capacity

The total volumetric capacity data shown in Figure 9 a) and b) are the as-reported capacities for Sample 1 and 2, respectively. The greyed-out data sets are not considered in the statistical analysis in Figure S6 and S7. Specifically, one participant had an outlier value for the packing density and was excluded; another reflects the incorrect free-gas volume calculation, and a third normalized the data by the wrong volume. We contacted the participating laboratories to correct these calculations. The re-submitted data is plotted in Figure 9 a) and b) and the interpolation of the re-submitted data is listed in the supplementary data. The statistical analysis for the total volumetric capacity at ambient temperature (Figure S6), shows very little variation in the capacities for either sample, due to the free-gas component dominating the total volumetric capacity. This occurs irrespective of the large variation that occurred with Sample 2's packing density determinations. This occurs irrespective of the large variation that occurred with Sample 2's packing density determinations. This occurs due to the fact that the packing volume appears in both the numerator and denominator in the calculation for the total volumetric capacity (see Eqns. 3 & 4).

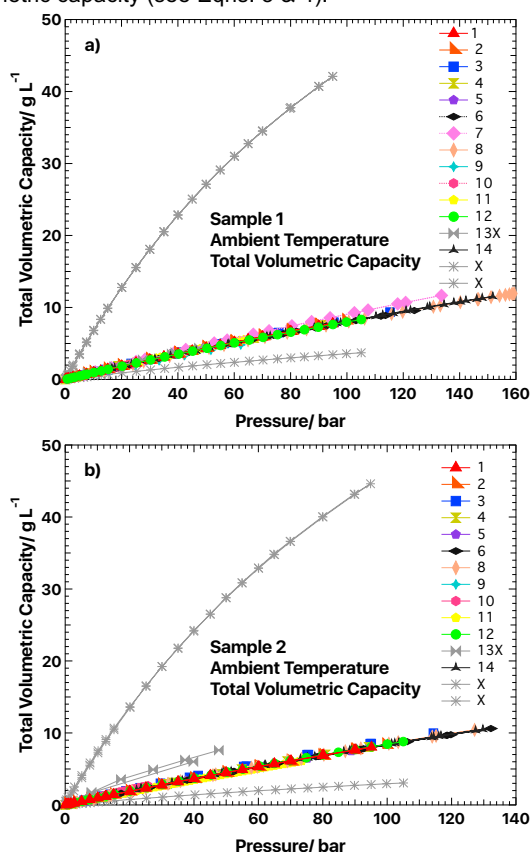


Figure 9. As-reported total volumetric capacities at ambient temperatures for a) Sample 1, and b) Sample 2.

The as-reported total volumetric capacities measured at liquid nitrogen temperature are shown in Figure 10 a) and b). The data shows good agreement for Sample 1 at low pressures up to 20 bar; at higher pressures, there are slight deviations, but generally good agreement. In contrast, the total volumetric capacity for Sample 2 shows a significantly larger variation (Figure S7). This can be attributed to the variation in the packing volume of Sample 2. The net decrease in precision is more

evident at liquid nitrogen temperatures with the much larger contribution of the adsorbed component versus the free-gas component e.g., the free-gas density is about 4 times larger at liquid nitrogen than at ambient temperatures, while the adsorbed component is approximately 200 times larger at low pressures and 6 times larger at high pressures. Hence, the excess capacity term contributes a significant amount for total volumetric capacity at liquid nitrogen temperatures which causes the variation in the packing density to influence the variation in total volumetric capacity.

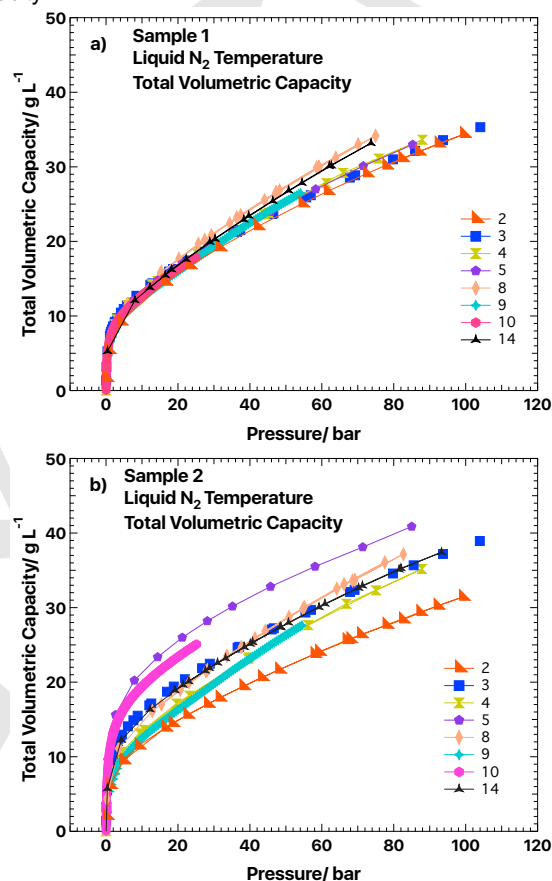


Figure 10. As-reported total volumetric capacities for a) Sample 1, and b) Sample 2.

In summary, we have found that variations in the packing density determinations can significantly influence the resultant volumetric capacity. This accentuates the need for accurate packing density measurements. Furthermore, it also suggests that standardized protocols for such measurements should be developed specifically for hydrogen-storage materials and/or explicit reporting on the exact methodology should be reported.

Discussion

The present study shows a marked improvement in the reproducibility of excess gravimetric hydrogen adsorption measurement on carbon powders compared to the Zlotea *et al.* report in 2009^[3]. We must note, the methodology of the statistical analysis and materials in the Zlotea study are different, therefore, a direct comparison of the specific results is not possible. To establish a meaningful comparison to the Zlotea study, we have used the interpolated data provided in the supplementary data to calculate the relative standard deviation, (*RSD*), according to

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equation 6 and 7. For the statistical analysis of Sample 1 and Sample 2, we have used the interpolated data values (Table S1 and S2) for all data sets using equations 6 and 7, where the mean value, (\bar{x}) is calculated based on the interpolated value (x) and the number of data sets (n). Figure 11 a) (ambient temperature) and 11 b) (liquid N₂ temperature) show a comparison of the RSDs for the gravimetric excess capacity of Sample 1 and Sample 2, with those of the Zlotea study.

$$\bar{x} = \frac{\sum x}{n} \quad (6)$$

$$RSD = \left(\frac{\sum (x - \bar{x})^2}{n - 1} \right)^{1/2} / \bar{x} \quad (7)$$

In general, the RSD for gravimetric excess capacity for ambient temperature is the highest at low pressures for all samples shown in Figure 11 a). Fundamentally, the mean amount of adsorption at low pressures is smallest in the Henry's law region of the isotherm. When the denominator in equation 7 is small, the RSD is magnified. Therefore, it is anticipated that the largest RSD occurs at low pressures for ambient temperatures when the adsorption amount is small. Although we did not inquire about the accuracy of the pressure transducers for each laboratory's instrument, it is likely that 1-2 bar is at the low operating range for high pressure transducers, and may not have high accuracy in this range. The RSD for Sample 1 at ambient temperature and 1 bar has a highest value at 54.6%. This value for Sample 1 at these conditions is based on 7 data sets, however the deviation is dominated by data set 13. This particular data set has an offset, such that if the amount of adsorption was extrapolated to zero bar, the y-intercept would not be zero. This non-physical behavior may be due to a mis-calibration at low pressures. The excess capacities for the six other data sets are clustered together at 1 bar. The highest RSD for Sample 2 is 31.2% at 2 bar. At these conditions, the RSD was more uniform amongst the data, and the greatest variation was spread among 4 out of 12 data sets. For pressures greater than 10 bar, the RSDs for Sample 1 and Sample 2 are roughly half that of the 2009 study. The same trends with pressure are also observed for measurements at liquid nitrogen temperature, Figure 11b). The RSD is not as high at low pressures for liquid nitrogen temperature since the amount of adsorption is much higher. Overall, the comparisons in Figure 11 depict a marked improvement in measurement reproducibility from the Zlotea 2009 measurement study. For example, at 15 bar, the RSD at ambient temperature decreased by 63% and 59% for Sample 1 and 2 respectively. At liquid nitrogen and 15 bar, the RSD decreased 61% and 90% for Sample 1 and 2 respectively. It is also important to note that the RSD for the 2009 study had removed data sets from their analysis, whereas the ILC18 (this study), has included all data in the analysis.

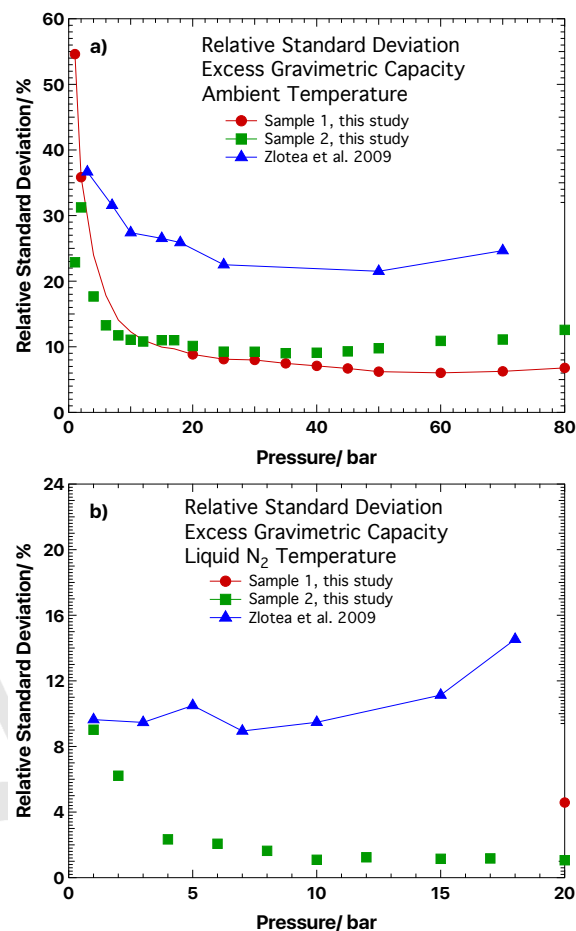


Figure 11. Comparison of the RSD of the gravimetric excess capacity for Sample 1, Sample 2, and a select set of data taken from a 2009 round robin study^[3]

In general, the excess and total volumetric capacities show a larger range of variation than gravimetric capacities which is attributed to differences in the packing densities. Data sets 5 and 10 reported the highest packing densities for Sample 2 (Figure 3), and subsequently report the highest values for excess (Figure 7 b) and total (Figure 10 b) volumetric capacities for Sample 2 at liquid nitrogen temperature.

For sorbent powders, compressed powders, or pellets, further guidelines are required to establish metrics for consistently measuring the packing density of materials. Standard test methods such as ASTM and ISO methods to measure the packing density of powders are often written specific to a particular material with specified shapes and physical dimensions. Based on empirical evidence, novel hydrogen storage materials often have heterogeneous morphologies with different electrostatic interactions. In the absence of such standards for hydrogen storage materials, it is important that the methods used to determine the packing density, and subsequent calculation of volumetric hydrogen storage capacities, are explicitly stated in reports. Until a standard test method is adopted by the hydrogen storage community, we recommend tapping powder samples by hand ~30 times in a graduated cylinder or equivalent. To prepare the sample for the characterization gas sorption properties, the material should be tapped in the sample holder using the same number of taps. Through the development of more rigorous methods for measuring the packing volume, consistent

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comparisons of the hydrogen volumetric capacities for different materials will continue to improve.

We expected to observe a trend linking smaller sample sizes with higher measurement uncertainties in the gravimetric excess capacities, however, this was not observed for Sample 1 or 2. The relative absolute deviation for the excess gravimetric capacity of Sample 2 was calculated at various pressures and compared with the corresponding sample mass for ambient temperature or liquid nitrogen temperature (Figure S8 a) and b)), and the values are listed in Tables S13 and S14 respectively). The ILC18 protocol encouraged the use of the largest sample size that each laboratory could experimentally accommodate. In this study, the smallest sample size measured was 0.184g. It is important to note that in general, manometric and gravimetric measurements are most accurate when the sample size is maximized. The measurement of small sample sizes results in the adsorption of a small number of gas moles which increases the uncertainty when compared to other sources of error. Therefore, the most accurate measurements are made in the region of higher adsorption measured with larger amounts of sample. Ultimately, the minimum sample mass is dependent upon the precision and accuracy of the specific instrument. The magnified variability for measuring a small number of moles is also observed at low pressures and ambient temperatures. This effect is noted in the RSD of the gravimetric excess capacities at low-pressure in Figure 11 a) for all 3 samples.

Conclusions

The packing volume is by far the most important variable in the uncertainty of the volumetric capacities found in this study, and identifying the role of other important parameters in this investigation is complex. There are factors that affect the accuracy of individual systems such as: control of the isothermal regions of the instrument, the calibration of the instrument, and the details of the mole balance calculations. Other factors that may contribute to the variability of data amongst different laboratories include the use of different equation of states, small temperature differences in “ambient” or “liquid nitrogen” temperatures, and variations in equilibrium times. In this study, we have tried to minimize the variables for sample preparation through defined degas conditions and measurement protocols, and through defined capacity calculations. We have reported some of the experimental differences of each laboratory (Table 1 and 2). The variability in the excess gravimetric capacities measured in this study reflect both individual instrument variability and inter-laboratory differences. We have shown the large variation in volumetric capacities is due to uncertainty in the measurement and/or real differences in the sample packing density.

The research community has made great progress in achieving a higher precision for excess gravimetric capacity measurements. Sample weight was not found to be a factor in the variability, however all measurements were done on samples 0.184g or larger. The largest variability amongst the data sets is observed for measurements of smaller amounts of adsorption, and these conditions occur at low pressures and ambient temperatures. Further investigations considering the correlations between measurement variability and various experimental parameters may yield interesting findings, however these investigations are beyond the scope of this report.

Our study has highlighted the need for more robust and universally accepted definitions and consistent measurement protocols for determining the packing density of sorbent materials in order to achieve more objective and uniform reporting of volumetric capacities. The packing density of a material can vary

due to sample preparation (compaction or tapping), particle morphology, and electrostatic interactions. In the absence of established protocols, we have recommended a tapping methodology and use of a graduated cylinder for measuring the volume. Most importantly, the conditions for measuring the packing volume should be explicitly stated, when reporting volumetric capacities. For future compaction studies of materials, it is important to note that Kunowsky *et al.* modelled the effect of the material's bulk density in relation to both the excess and total volumetric capacities.^[26] When the bulk density increases, the volume fraction occupied by the atoms that comprise the material increase, leading to a smaller void volume and higher volumetric capacity. Therefore, compaction may be an alternative path forward for hydrogen storage materials.

Outlook

Moving forward, our attention now turns to enhancing the reproducibility of volumetric capacities, and finding robust and universally accepted definitions and protocols for measuring the packing density of sorbent materials needed to accurately describe hydrogen volumetric capacities. Important studies to investigate effects of the packing volume, compression and compaction are needed to maximize the total volumetric capacities to reach the DOE storage goals. Ideally, a high capacity sorbent material will minimize the free-gas volume, and future efforts will likely focus on this approach. A number of reports have investigated the densification of powder sorbents in order to minimize the free-gas contribution and increase volumetric capacities, using activated carbon fibers, MOF-5,^[27] MOF-5 combined with expanded natural graphite,^[28] MIL 101,^[29, 30] and MOF-177.^[31] However, there is a material-dependent compression pressure in which the pore structure will collapse if the sample is compacted too much.^[27] Theoretical investigations have provided a path forward by correlating important physical parameters of materials (i.e. pore volume, surface area, volumetric surface area) with maximizing volumetric hydrogen capacities.^[21, 32, 33]

Conflicts of interest

There are no conflicts to declare.

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Table 1. EXPERIMENTAL DETAILS FOR SAMPLE 1 MEASUREMENTS

CODE	METHOD [A]	LOW T (K)	HIGH T (K)	SKELETAL DENSITY (G/CM ³)	PACKING DENSITY (G/CM ³)	FINAL MASS (G)	MASS LOSS (%)	DEGAS PRES. (BAR)	EQUILIBRIUM TIME LOW T (MIN.)	EQUILIBRIUM TIME HIGH T (MIN.)	NON-IDEALITY CALCULATION
1	V	NM ^[B]	298	2.309	0.352	3.467	1.00	1E-6	30	30	HELMHOLTZ
2	V	77	298	2.15	0.352	0.633	3.59	1E-6	15	15	HELMHOLTZ
3	V	77	292	2.1	0.38	1.424	3.02	<5E-6	5	5	NR ^[D]
4	V	77	298	2.4	0.37	1.45	0.69	1E-9	5	5	GASPAK V3.32
5	V	77	298	2.1 ^[C]	0.362	0.8	0.00	1E-9	10	10	REFPROP ^[I]
6	V	76	303	2.293	0.345	0.987	2.15	1E-10	10	30	GASPAK V3.31
7	V	NM ^[B]	303	NR ^[D]	0.336	0.323	5.47	1E-10	10	20	GASPAK V3.31
8	V	76	303	2.3	0.350	0.429	3.49	1E-10	10	30	GASPAK V3.31
9	V	77	298	1.42	0.36	0.413	0.44	3.6E-3	30	30	GASPAK
10	V	77	297	2.185	0.365	0.231	2.19	1E-8	1	1	^[G]
11	V	NM ^[B]	303	2.29	0.351	1.850	NR ^[D] J	1E-6	NM ^[B]	^[E]	REFPROP ^[H]
12	V	NM ^[B]	298	2.223	0.354	1.420	2.41	5E-5	NM ^[B]	30	MBWR
13	V	NM ^[B]	297	1.98	0.531	1.093	0.23	-4E-9	NM ^[B]	60	^[F]
14	V	76	303	2.229	0.354	0.333	10.2	1E-10	10	30	GASPAK V3.31
15	G	77	295	2.331	NM ^[B]	0.184	2.00	7E-10	60	60	NR ^[D]

[A] V – VOLUMETRIC MEASUREMENT, G – GRAVIMETRIC MEASUREMENT

[B] NM – NOT MEASURED

[C] ASSUMED

[D] NR - NOT REPORTED

[E] EQUILIBRIUM TIME WAS REPORTED BASED ON CHANGE IN PRESSURE OVER TIME OF 8.3E-6 BAR/S

[F] FIT REAL PRESSURE (BAR) DATA: $(-5.73258e-8 \cdot T^2 + 1.634392e-5 \cdot T - 0.002622676) \cdot (P \cdot 1e-5)^2 + (5.163314e-6 \cdot T^2 - 0.001678522 \cdot T + 0.441234) \cdot (P \cdot 1e-5)$ [G] ^[34][H] ^[35]

[I] MBWR EQUATION OF STATE

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Table 2. EXPERIMENTAL DETAILS FOR SAMPLE 2 MEASUREMENTS

CODE	METHOD [A]	LOW T (K)	HIGH T (K)	SKELETAL DENSITY (g/cm ³)	PACKING DENSITY (g/cm ³)	FINAL MASS (G)	MASS LOSS (%)	DEGAS PRES. (BAR)	EQUILIBRIUM TIME LOW T (MIN.)	EQUILIBRIUM TIME HIGH T (MIN.)	NON-IDEALITY CALCULATION
1	V	NM ^[B]	297	2.407	0.191	2.0085	2.18	1E-6	NM ^[B]	30	HELMHOLTZ
2	V	77	298	3.17	0.207	0.3099	4.26	1E-6	15	15	HELMHOLTZ
3	V	77	292	2.1	0.29	1.08	2.17	<5E-6	5	5	NR ^[D]
4	V	77	298	2.6	0.23	1.03	0.971	1E-9	5	5	GASPAK V3.32
5	V	77	298	2.1 ^[C]	0.412	0.475	1.684	1E-9	10	10	REFPROP ^[I]
6	V	NM ^[B]	303	2.28	0.2422	0.9356	NR ^[D]	1E-10	NM ^[B]	20	GASPAK V3.31
8	V	76	303	2.3	0.3501	0.204	2.3	1E-10	10	30	GASPAK V3.31
9	V	77	298	1.56	0.22	0.3843	0.598	1E-10	30	30	GASPAK
10	V	77	297	2.3094	0.3784	0.23352	0.45	3.6E-3	1	1	^[G]
11	V	NA	303	2.369	0.176	0.890	NR ^[D]	1E-8	NM ^[B]	^[E]	REFPROP ^[H]
12	V	NM ^[B]	298	2.384	0.242	1.420	2.30	1E-6	NM ^[B]	30	MBWR
13	V	NM ^[B]	197	3.28	1.05	0.2994	^[J]	5E-5	NM ^[B]	60	^[F]
14	V	76	303	2.123	0.273	0.7823	1.59	-4E-9	10	30	GASPAK V3.31
15	G	77	295	2.3305	NM ^[B]	0.18270	2.00	1E-10	60	60	NR ^[D]

[A] V – VOLUMETRIC MEASUREMENT, G – GRAVIMETRIC MEASUREMENT

[B] NM – NOT MEASURED

[C] ASSUMED

[D] NR - NOT REPORTED

[E] EQUILIBRIUM TIME WAS REPORTED BASED ON CHANGE IN PRESSURE OVER TIME OF 8.3E-6 BAR/S

[F] FIT REAL PRESSURE (BAR) DATA: $(-5.73258e-8 * T^2 + 1.634392e-5 * T - 0.002622676) * (P * 1e-5)^2 + (5.163314e-6 * T^2 - 0.001678522 * T + 0.441234) * (P * 1e-5)$ [G] ^[34][H] ^[35]

[I] MBWR EQUATION OF STATE

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