**Compaction: A mechanochemical approach to carbons with
superior porosity and exceptional performance for hydrogen and
CO₂ storage**

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Abstract

We describe a compactation approach, which incorporates a mechanical compression step before thermochemical activation, to carbons that possess higher porosity than analogous conventionally activated carbons but without any significant changes in pore size. The method works for both highly activated and lowly activated carbons. For highly compactivated carbons (thermal treatment at 800 °C), enhanced porosity (surface area and pore volume up to 4000 m² g⁻¹ and 3.0 cm³ g⁻¹) is achieved along with superior hydrogen uptake of 7.3 wt% (at -196°C and 20 bar), rising to 9.6 wt% at 40 bar and 14.2 wt% at 150 bar, which corresponds to volumetric uptake of 38 g l⁻¹ at 40 bar and 56 g l⁻¹ at 150 bar, while at room temperature uptake reaches 3.6 wt% (14 g l⁻¹). On densification, the highly compactivated carbons can retain a much greater proportion of their porosity (3200 – 3500 m² g⁻¹ and 2.0 – 2.7 cm³ g⁻¹) whilst attaining high packing density, which translates to exceptional volumetric hydrogen storage; 49 g l⁻¹ at 40 bar, 60 g l⁻¹ at 80 bar and 72 g l⁻¹ at 150 bar and -196 °C, while at room temperature and 150 bar the densified carbons can store 3.4 wt% (18 g l⁻¹). For lowly activated carbons (thermal treatment at 600 °C), compactation yields carbons with 35% higher surface area and pore volume but with no pore size expansion. The increase in surface area arising from small (5.9 Å) micropores results in a dramatic increase in CO₂ storage capacity; at 25 °C the CO₂ uptake rises from 1.3 to 2.1 mmol g⁻¹ at 0.15 bar, and from 3.4 to 5.5 mmol g⁻¹ at 1 bar. Due to their lowly activated nature, the highly microporous compactivated carbons have high packing density and thus exhibit very high volumetric CO₂ uptake of 79 g l⁻¹ and 206 g l⁻¹ at 0.15 and 1 bar, respectively (cf to 52 g l⁻¹ and 136 g l⁻¹ for conventionally activated analogue).

Keywords: compactation; mechanochemical; activated carbon; hydrogen storage; CO₂ storage; densified

1. Introduction

Activated carbons are one of the most widely used and studied classes of porous materials [1-7]. Their abundance, physical and chemical stability along with a typically high surface area ($> 1000 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($> 0.5 \text{ cm}^3 \text{ g}^{-1}$) is attractive and engenders their suitability for a wide range of applications, for example, as adsorbents, catalyst supports and storage materials [1-7]. Activated carbons are prepared via the so-called activation process wherein non-porous or lowly porous carbonaceous matter (the carbon precursor) is exposed to treatment that generates pore channels and constrained spaces (i.e., porosity) that permeate the whole material [1-7]. The activation process acts by either generating, increasing or transforming porosity within the carbon precursor as measured by key indicators, namely, surface area, pore volume and pore size distribution (PSD). The preparation of activated carbons from a wide variety of carbonaceous precursors, such as biomass, coal, lignite coke, biochar or carbon rich polymers, can be performed in two ways [6]: (i) physical activation at $500 - 1200 \text{ }^\circ\text{C}$ with activating agents such as air, O_2 , CO_2 , steam or their mixtures, or (ii) chemical activation under inert atmosphere at $500 - 900 \text{ }^\circ\text{C}$ with reagents such as KOH, NaOH, H_3PO_4 or ZnCl_2 as activating agents. Among the various activating agents, KOH is known to generate carbons with high surface area ($> 2000 \text{ m}^2 \text{ g}^{-1}$) and high pore volume ($\sim 1.5 \text{ cm}^3 \text{ g}^{-1}$) from a variety of carbon precursors such as hydrothermally carbonized carbon [6,7], carbon rich polymers [8,9], petroleum coke [10], CDCs [11,12], zeolite-templated carbon (ZTC) [13], other forms of templated carbons [14], and graphene [15].

Several parameters are known to determine the extent and type of porosity generated in KOH activated carbon, including (i) the KOH/carbon mass ratio, (ii) the activation temperature, (iii) activation duration and (iv) the mixing procedure (solution or mechanical mixing) [6], with the first two (amount of KOH and temperature) being the most important. Greater amounts of KOH activating agent can result in increased porosity but usually at the

expense of pore size uniformity, i.e., widening of the PSD. It is, however, highly desirable to reduce both the activation temperature and amount of activating reagent required to achieve any given level of porosity. One major limitation of KOH-based carbon activation process is that in most cases the KOH and carbon precursor are initially *both* solids. This means that the activation process is predicated initially on solid-solid interactions between particulates of KOH and carbon, which means the mixing and activation process, once the activating agent melts, can be slow and inefficient thus requiring higher temperature and higher amounts of activating agent to achieve a given level of activation and porosity. The mechanical mixing of KOH and carbon can only at best place the respective (KOH and carbon) particles loosely close to each other. This scenario does not exclude the possibility that some of the KOH may be inefficiently used and that the carbon particles may be unevenly activated depending on the level of mixing and contact. A possible remedy is to increase contact between the particles of the KOH and carbon prior to the thermal activation process. Closer contact can be achieved by reducing interparticle voids via compaction of KOH/carbon mixtures into pellets or disks prior to thermochemical treatment. Here we explore the effect of such compaction on the carbon activation process and show that it is possible to significantly improve the level of activation and porosity generated, especially at lower KOH/carbon ratio, but without any deleterious effects on pore size and pore size distribution. We show that incorporation of a mechanical compression step prior to thermochemical activation (a process for which we have coined the term compactivation), achieves significantly higher levels of porosity (surface area and pore volume) at any given KOH/carbon ratio and temperature, and that the resulting, so-called compactivated carbons, have exceptional hydrogen and CO₂ storage capacity.

2. Experimental

2.1. Materials synthesis

2.1.1. Carbon precursors

Polypyrrole (PPy) was prepared using FeCl_3 as oxidant. In a typical synthesis, pyrrole (3 g), recently distilled under nitrogen, was added to a solution of FeCl_3 (0.5 M, 200 mL) and the mixture was magnetically stirred for 2 h. The resulting product was separated by filtration and washed with distilled water and dried. The polypyrrole yield was close to 100%. The polypyrrole had elemental composition (wt%) of; C (65.2), H (4.4) O (16.7), N (13.4), S (0.2). Wood sawdust derived biochar was prepared as follows; an aqueous dispersion of sawdust (320 g l^{-1}) was placed in a stainless steel autoclave and heated at 250°C for 2 h. The resulting solid (hydrochar) was recovered by filtration, washed with distilled water and dried at 120°C for 4 h. The elemental composition of the hydrochar was (wt%); C (69.3), H (6.8), O (23.9).

2.1.2. Compactation and conventional activation

In a typical compactation process, the carbon precursor was thoroughly mixed with KOH at the desired ratio (KOH/carbon ratio of 2, 3 or 4) in an agate mortar. The KOH/carbon mixtures was then compacted for 10 min at load of 10 tonnes in a 1.3 cm diameter die, equivalent to compaction pressure of 740 MPa. The resulting disks/pellets, in an alumina boat, were placed in a horizontal furnace and heat treated to the target activation temperature (600 or 800°C) at heating ramp rate of 3°C/min under a nitrogen gas flow and held at the desired temperature for 1 h. The resulting compactivated carbons were then thoroughly washed several times with 10 wt% HCl to remove any inorganic salts, and then washed with distilled water until neutral pH. No stirring was used during the washing step. Finally, the compactivated carbons were dried in an oven at 120°C for 3 h.

Conventionally activated carbons were prepared as described above but without the compaction step.

2.2. Materials Characterisation

2.2.1. Porosity analysis

Nitrogen sorption isotherms and textural properties of the activated and compactivated carbons were determined at -196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer. Prior to analysis, the carbons were pre-dried in an oven at 120 °C and then degassed overnight at 200 °C under high vacuum. The surface area was calculated using the BET method based on adsorption data in the relative pressure (P/Po) range 0.04 to 0.2 and total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore surface area and micropore volume were estimated by t-plot analysis. The pore size distribution (PSD) was determined using a Non Local Density Functional Theory (NLDFT) model using nitrogen adsorption data.

2.2.2. Gas uptake measurements:

Hydrogen uptake capacity of the carbons was measured by gravimetric analysis with an Intelligent Gravimetric Analyser, IGA-003, (Hiden) using 99.9999% purity hydrogen additionally purified by a molecular sieve filter. Prior to analysis, the carbon samples were dried in an oven at 80 °C for 24 h and then placed in the analysis chamber and degassed at 200 °C and 10^{-10} bar for 4 – 6 h. The hydrogen uptake measurements were typically performed at -196 °C (in a liquid nitrogen bath) over the pressure range 0 to 20 bar. Hydrogen uptake was also performed on a Hiden Xemis Analyser at -196 °C and room temperature in the pressure range 0 – 150 bar.

CO₂ uptake measurements were performed over the pressure range of 0 – 20 bar with a Hiden intelligent gravimetric analyzer (IGA-003). The carbon samples were outgassed under vacuum at 250 °C before analysis. Then the CO₂ uptake isotherms were measured at room temperature in the pressure range 0 – 20 bar.

3. Results and Discussion

3.1. Porosity

3.1.1. High levels of activation: thermochemical treatment at 800 °C

We used two contrasting carbon precursors as starting materials, namely, (i) the carbon rich polymer, polypyrrole (PPy), which is known to yield high surface area ($\sim 3000 \text{ m}^2 \text{ g}^{-1}$) activated carbons [9], and (ii) biomass (i.e., wood sawdust) biochar for which the highest surface area obtained so far is limited to less than $3000 \text{ m}^2 \text{ g}^{-1}$ [16]. The nitrogen sorption isotherms and corresponding PSD curves of PPy-derived activated carbons (designated as PPYx, where x is KOH/PPy ratio) and equivalent compactivated carbons (designated as MPPYx), prepared at activating temperature of 800 °C and a KOH/PPy ratio of 2, 3 and 4 are shown in Figure 1a-c. The compactivated carbons adsorb higher amounts of nitrogen compared to equivalent activated carbons, and both sets of samples have significant adsorption at very low relative pressure ($P/P_0 < 0.01$). The isotherms show a linear increase in adsorption in the P/P_0 range of 0.1 to 0.4, which indicates the presence of super-microporosity and mesoporosity. Despite the higher nitrogen sorption for compactivated (MPPYx) samples, there is hardly any change in the shape of the isotherm, meaning that the activated and compactivated carbons have similar pore size distribution; PSD curves (Inset Figure 1a-c) show that the size of pores generated in the activated and compactivated carbons is comparable. This is an unusual finding since higher levels of porosity in activated carbons are usually accompanied by the formation of larger pores [6]. We also confirmed (Supporting Figure S1) that the compactivation process did not alter the presence and/or distribution/proportion of larger pores (mesopores and/or macropores); the wider range pore size distribution is similar for both activated and compactivated sets of samples. The wider range pore size distribution plots also indicated that the porosity of the MPPYx and PPYx samples is mainly from micropores and small mesopores (up to $60 \text{ \AA}$) range (Figure 1 and

supporting Figure S1). Furthermore, despite higher levels of porosity, the carbon yield for the compactivated carbons was comparable to that of equivalent conventionally activated carbons (Supporting Table S1) and generally within the range expected for activated carbons derived from polypyrrole [6,9]. A carbon yield of 14 - 23% is comparable or higher than that achieved for high surface area activated carbons that are prepared via physical activation [6].

Figure 1. Nitrogen sorption isotherms and corresponding pore size distribution (PSD) curves (inset) of polypyrrole-derived activated (PPY_x) and compactivated (MPPY_x) carbons prepared at 800 °C and KOH/PPy ratio of; (a) 2, (b) 3 and (c) 4, and (d) wood sawdust-derived activated carbon (S4800) and compactivated carbon (S4800P) prepared at 800 °C and KOH/carbon ratio of 4. The PSD curves of compactivated carbons are offset (y-axis) by 0.1 cm³ g⁻¹.

The textural parameters of the activated and compactivated carbons prepared at 800 °C are summarised in Table 1. The improved porosity achieved via compactivation is particularly evident at lower KOH/PPy ratio. Thus, the surface area of activated PPY2 is 2360 m² g⁻¹ compared to 3321 m² g⁻¹ for the compactivated MPPY2 sample, which represents a 41% increase. At KOH/PPy ratio of 3 and 4, the enhancement in surface area for compactivated carbons over equivalent activated analogues is 12% and 19%, respectively. Compactivation generates a carbon with surface area of 3844 m² g⁻¹, which is much higher than that of conventional activated carbons [1-17]. As stated above, the KOH/carbon ratio is one of the most important parameters in determining the extent and nature (i.e. pore size) of porosity in activated carbons (Supporting Figure S2). As illustrated for PPy-derived activated carbons (Supporting Figure S2), increase in porosity is usually accompanied by increase in pore size. It is noteworthy that compactivation generates, at KOH/PPy ratio of 2, a carbon (MPPY2) with surface area (3321 m² g⁻¹) that is comparable to that (3225 m² g⁻¹) achieved at KOH/PPy ratio of 4 via conventional activation (sample PPY4). This means that to generate similar surface area, compactivation requires only half the amount of KOH compared to conventional activation, which translates to a more efficient use of the activating agent. The pore size data in Table 1 confirms that there is hardly any change in the size of pores generated in activated and compactivated carbons despite the higher porosity of the later. The pore volume data in Table 1 also confirms that in all cases the compactivated (MPPYx) samples have higher pore volume compared to equivalent activated (PPYx) samples, with sample MPPY4 reaching a very high pore volume of 2.89 cm³ g⁻¹, which is amongst the highest ever reported for activated carbons [6,11,17]. Indeed, when benchmarked against a commercially available high surface area (i.e., 2881 m² g⁻¹) and pore volume (1.71 cm³ g⁻¹) carbon (AX21), sample MPPY4 is superior in terms amount of nitrogen adsorbed and overall porosity despite relatively similar pore size distribution (Supporting Figure S3).

Table 1. Textural properties and hydrogen uptake of highly activated and compactivated carbons prepared at 800 °C.

Sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (Å) ^a	H ₂ uptake ^b (wt%)	
				Excess	Total
PPY2	2360	1.53	12/25	3.3	4.3
MPPY2	3321	1.76	12/22	4.8	6.0
PPY3	3067	1.58	12/26	4.8	5.8
MPPY3	3442	2.05	12/28	5.4	6.8
PPY4	3225	2.43	13/34	5.0	6.5
MPPY4	3844	2.89	13/34	5.5	7.3
S4800	2797	1.74	8/12/28	5.0	6.1
S4800P	3951	2.47	8/12/28	5.5	7.1

^aMaxima of pore size distribution obtained using non-local density functional theory (NLDFT) analysis. ^bExcess or total hydrogen uptake capacity at -196 °C and 20 bar.

The porosity data discussed above points to a scenario where compaction of KOH/carbon precursor mixtures before thermochemical treatment offers clear benefits of increased porosity without compromising or changing the pore size of the resulting carbons. Furthermore, the N content of the two sets of carbons, activated and compactivated is similar; ca. 0.4 wt% for PPY4 and MPPY4, 0.55 wt% for PPY3 and MPPY3 and ca. 0.75 wt% for PPY2 and MPPY2, which is in agreement with what has previously been reported for comparable PPY-derived activated carbons [9]. The benefits of compactivation are particularly stark at 800 °C and low KOH/PPy ratio. It is likely that the solid-solid nature of the activation process during the early stages of the thermal treatment step, prior to melting of the KOH activating agent, is enhanced by the close KOH-carbon interparticle contact that is afforded by the compaction. For highly activated carbons (activated at 800 °C), the benefits of the compaction step with respect to porosity are accompanied by some subtle changes in the

nature of the carbon with respect to graphitisation as shown by powder XRD analysis (Supporting Figure S4) and Raman spectra (Supporting Figure S5). Although the highest surface area carbons are largely amorphous, the level of graphitisation, as suggested by both powder XRD analysis and Raman spectra (Supporting Figures S4 and S6) is lower for the compactivated carbons, which is consistent with their higher porosity. The level of structural order/disorder in the compactivated carbons is similar to that of activated carbons according to TEM images (Supporting Figure S6). Furthermore, the particle morphology of equivalent compactivated and activated samples was largely similar and comparable to other types of activated carbons generated via KOH activation [16]. Sharp edged continuous platy aggregates similar to those previously reported for biomass-derived carbons were observed [16].

To explore the general applicability of the compactivation process, we also used hydrochar derived from wood sawdust [16,17] as precursor for activation at 800 °C and KOH/carbon ratio of 4. The nitrogen sorption isotherms in Figure 1d show similarly shaped isotherms for the activated (S4800) and compactivated (S4800P) wood sawdust-derived samples, but with much higher nitrogen adsorption for the later. As shown in Table 1, the activated S4800 sample has a surface area of 2797 m² g⁻¹, which is at the limit of what is obtainable for such materials [16], compared to 3951 m² g⁻¹ for the compactivated S4800P sample. A surface area of 3951 m² g⁻¹, which is a 41% increase over the activated sample, is at the limit of what has been reported for carbons [6], and in particular for KOH-activated carbons derived from biomass [16]. The pore volume of S4800P (2.47 cm³ g⁻¹) is also 42% higher than that of S4800 (1.74 cm³ g⁻¹). It is noteworthy that despite possessing higher porosity, the compactivated S4800P sample exhibits comparable PSD to the activated S4800 sample (inset Figure 1d). The micropore surface area (obtained using t-plot analysis; Supporting Figure S7) of the compactivated S4800P sample (1413 m² g⁻¹) is slightly higher

than that of the activated S4800 equivalent ($1157 \text{ m}^2 \text{ g}^{-1}$), which means that the proportion of microporosity remains largely unchanged at ca. 40% for both samples. Thus the increase in total porosity is not at the expense of microporosity.

3.1.2. Low levels of activation: thermochemical treatment at 600 °C

With a view of generating materials suitable for post-combustion CO_2 capture where small micropores of size $< 10 \text{ \AA}$ are necessary [18-20], we explored the effect of compactivation at lower levels of activation by preparing polypyrrole-derived samples at 600 °C and KOH/PPy ratio of 2; the activated carbon was designated as PPY2600 and the compactivated carbon as MPPY2600. The nitrogen sorption isotherms and corresponding PSD curves of the lowly activated and compactivated carbons are shown in Figure 2. The sorption isotherm of the compactivated MPPY2600 sample has higher nitrogen adsorption compared to the conventionally activated PPY2600 carbon. However both samples are highly microporous as indicated by their significant nitrogen sorption at $P/P_0 < 0.01$. The textural parameters in Table 2 confirm the higher porosity of the compactivated carbon; the surface area and pore volume of the MPPY2600 carbon is ca. 35% higher than for activated PPY2600. The surface area rises from $976 \text{ m}^2 \text{ g}^{-1}$ to $1297 \text{ m}^2 \text{ g}^{-1}$, while pore volume increases from $0.47 \text{ cm}^3 \text{ g}^{-1}$ to $0.64 \text{ cm}^3 \text{ g}^{-1}$. Despite this increase in porosity, there is no pore size expansion for sample MPPY2600, but rather there is a slight reduction in the size of the main pore channels from 6.8 to 5.9 $\text{\AA}$. However, overall the PSD remains largely similar over the pore size range up to 800 $\text{\AA}$ (Figure 2 and Supporting Figure S8). As shown in Table 1, the level of microporosity is similar for both samples at ca. 92% of surface area and 85% of pore volume. Furthermore, the N content of the samples was similar; 12.4 and 12.2 wt% for PPY2600 and MPPY2600, respectively, compared to 13.4 wt% for the starting polypyrrole. Thus compactivation

provides a synthesis route for preparing highly microporous carbons with enhanced surface area but with no change to two other key properties; pore size and N content.

Figure 2. Nitrogen sorption isotherms (A) and pore size distribution (PSD) curves (B) of polypyrrole-derived (PPY) compactivated carbon (MPPY2600) and conventionally activated (PPY2600) carbon prepared at 600 °C and KOH/PPY ratio of 2.

Table 2. Textural properties and CO₂ uptake of polypyrrole-derived compactivated (MPPY2600) and conventionally activated (PPY2600) carbons.

Sample	Surface area ^a (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore size ^c (Å)	CO ₂ uptake ^d (mmol g ⁻¹)		
				0.15 bar	1 bar	20 bar
PPY2600	976 (906)	0.47 (0.40)	6.8	1.3	3.4	8.5
MPPY2600	1297 (1183)	0.64 (0.53)	5.9	2.1	5.5	13.2

The values in the parentheses refer to: ^aMicropore surface area and ^bmicropore volume. ^cMain pore size distribution maxima obtained from NLDFT analysis. ^dCO₂ uptake at 25 °C and various pressures (i.e., 0.15, 1 bar and 20 bar).

3.2. Hydrogen storage: Highly activated and compactivated carbons

Porous carbons are currently the subject of intensive research efforts aimed at gauging their potential for hydrogen storage [21]. Research efforts are informed by the need to generate carbons with the highest surface area and suitably large pore volume arising from appropriately sized pores. To date, the best performing carbon materials are zeolite template carbons [22-24], carbide-derived carbons (CDCs) [25,26], or activated carbons [6,27,28,29]. However, majority of studies to date report moderate hydrogen uptake (3.0 – 5.2 wt% at -196 °C and 20 bar) for activated carbons [5,6,30]. Currently, the best activated carbon stores are (i) doubly (physical and KOH activation) activated carbon with uptake of 7.08 wt% [27], (ii) PPy-derived activated carbons with uptake of 7.03 wt% [9], and low temperature synthesized activated CNTs with uptake of 7.3 wt% [29], at -196 °C and 20 bar. The hydrogen storage capacity of the present activated and compactivated carbons was investigated at -196 °C and room temperature using a gravimetric method on either a Hiden Intelligent Gravimetric Analyser (IGA 003) in the pressure range 0 – 20 bar or a Hiden Xemis analyser (pressure range 0 – 150 bar). The veracity of hydrogen storage data obtained from our IGA has previously been validated by comparison with volume-based measurements from other labs [22]. Figure 3 shows the excess and total hydrogen uptake isotherms for highly activated and compactivated carbons, and the uptake at 20 bar is summarised in Table 1. Excess uptake is the amount of hydrogen adsorbed in the carbons above that which would have been stored in the pores under similar conditions (temperature and pressure) assuming zero energy of interaction between the hydrogen and the carbon pore walls. The total uptake, on the other hand, is calculated from the excess storage by taking into account the amount of hydrogen compressed into the carbon pore volume space. Our gravimetric methods measured the excess hydrogen uptake from which the total storage, which is the more relevant value from an

application point of view, was obtained using established procedures (see Supporting information for details) [28,31].

Figure 3. Excess and total hydrogen uptake of polypyrrole-derived activated (PPY_x) and compactivated (MPPY_x) carbons prepared at 800 °C and KOH/PPy ratio of; (a) 2, (b) 3 and (c) 4, and (d) wood sawdust-derived activated carbon (S4800) and compactivated carbon (S4800P) prepared at 800 °C and KOH/carbon ratio of 4.

The hydrogen uptake is reversible, with no hysteresis, and no saturation is attained in the 0 – 20 bar pressure range. In all cases, the uptake of the compactivated carbons is higher than that of the analogous activated carbon, which is consistent with the higher porosity of the former set of samples. For example, at -196 °C and 20 bar, the excess and total hydrogen uptake of the activated PPY2 sample is 3.3 and 4.3 wt%, respectively, compared to 4.8 and 6.0 wt% for the compactivated MPPY2 sample; the excess hydrogen storage of MPPY2 is 45% higher, while the total uptake is enhanced by 40%. This increase in hydrogen storage closely matches the 41% increase in surface area engendered by compactivation as discussed above. This trend is consistent with recent findings that established the fact that, for carbons with similar pore size distribution, the hydrogen uptake can scale with surface area [32]. Similar trends in hydrogen storage capacity are observed for the other PPy and wood sawdust derived samples as shown in Figure 3 and Table 1. It is noteworthy that at -196 °C and 20 bar, the compactivated MPPY4 and S4800P samples have total hydrogen uptake of 7.3 wt% and 7.1 wt%, which are amongst the highest ever reported for activated carbons [5,6,9,16,21,27-30]. Amongst all carbons, such hydrogen storage capacity is only matched by zeolite-templated carbons [22-24]. For benchmarking purposes, we performed hydrogen uptake on a commercially available high surface area carbon, AX21, and compared it to the activated PPY4 and compactivated MPPY4 samples (Supporting Figure S9). The hydrogen uptake of AX21; excess and total uptake of 4.5 wt% and 5.6 wt%, respectively is similar to what has previously been measured under volumetric conditions [33]. This, firstly, further confirms the veracity of our gravimetric hydrogen uptake measurements and that they are comparable to what is obtained via volumetric approaches [33]. Secondly, it is clear that the compactivated MPPY4 sample has much higher hydrogen uptake than the benchmark carbon AX21 (Supporting Figure S9). Our hydrogen storage data was additionally verified by comparison with deuterium uptake (Supporting Figure S10A), wherein the expected wt% uptake ratio of

2:1 ($\text{D}_2\text{:H}_2$) was observed (Supporting Figure S10B). Moreover the observed molar ratio of adsorbed $\text{D}_2\text{:H}_2$ was close to unity and generally varied in the range 1.05 – 1.12 (Supporting Figure S10B), which is in agreement with what has previously been reported (i.e., molar ratio of 1.06 – 1.10) for comparable porous carbons under cryogenic conditions [34,35].

3.3.1. Densification

The on-going search for suitable hydrogen stores for vehicular on-board applications is aimed at finding materials that can achieve targets set at levels that would allow commercially viable and practical usage [21]. The most commonly quoted targets are those set by the United States Department of Energy (DOE); namely, a system gravimetric uptake capacity of 5.5 wt% and volumetric uptake capacity of 40 g l^{-1} by 2020, and ultimate targets of 7.5 wt% (system gravimetric storage capacity) and 70 g l^{-1} (volumetric uptake capacity) [36]. This means that besides gravimetric uptake, the volumetric hydrogen storage capacity is equally important. Whilst the gravimetric hydrogen uptake depends on the porosity of the adsorbent, the volumetric uptake is significantly affected by the packing density. Indeed, many porous materials that have attractive gravimetric hydrogen uptake are not viable due to their low volumetric uptake, which is occasioned by inherently low packing density [37,38]. The simplest way to increase the volumetric hydrogen uptake of porous materials is via densification (i.e.; compaction) processes wherein there is no associated decrease in porosity or gravimetric hydrogen uptake. We therefore explored the effect of densification on the porosity of PPy-derived activated and compactivated carbons. To achieve densification, the carbons were compacted at a load of 5 tonnes (370 MPa) or 10 tonnes (740 MPa), i.e., 5 and 10 tonne load in a 1.3 cm diameter die. The densified samples were designated as “sample name-C5” and “sample name-C10” after compaction at 370 and 740 MPa, respectively.

Figure 4 shows the nitrogen sorption isotherms and corresponding PSD curves for activated PPY4 and compactivated MPPY4 carbons before and after densification. The isotherms show that; (i) densification causes a decrease in the amount of nitrogen adsorbed, (ii) the decrease in porosity is higher at 740 MPa than at 370 MPa and, crucially, (iii) that the compactivated MPPY4 sample (Figure 4a) retains a much higher proportion of porosity than the activated PPY4 carbon (Figure 4c). Densification at 740 MPa causes a drastic reduction in amount of nitrogen adsorbed by activated sample PPY4, while the decrease is more modest for compactivated MPPY4. The PSD curves (Figure 4b and d) indicate that the pore size of the carbons is largely unchanged after densification at both 370 and 740 MPa. The textural properties after densification are given in Table 3 and indicate only a slight reduction in the size of mesopores but with no change to micropores. For the activated PPY4 sample, densification at 370 MPa decreases the surface area and pore volume by 15 and 22%, respectively, while for sample MPPY4 the reductions are lower at 13 and 11%, respectively. Densification at 740 MPa caused a significant reduction in the porosity of the activated PPY4 sample; the surface area reduced by 36% (from 3225 to 2060 m² g⁻¹), while the pore volume was lowered by 47% from 2.43 to 1.30 cm³ g⁻¹. On the other hand, the compactivated MPPY4 sample exhibited much greater stability after densification at 740 MPa; the surface area reduced by only 17% (from 3844 to 3174 m² g⁻¹), while the pore volume was lowered by just 28% from 2.89 to 2.09 cm³ g⁻¹. Indeed, surface area and pore volume above 3000 m² g⁻¹ and 2 cm³ g⁻¹, respectively, are remarkable for an activated carbon densified at high compression pressure of 740 MPa [39]. We attribute the mechanical stability to the fact that the compactivated carbons were already compressed during synthesis. As shown in Table 3, the decrease in porosity after densification at 740 MPa results in 10% decrease in gravimetric hydrogen uptake (5.0 to 4.5 wt% for excess, and 6.5 to 5.9 wt% for total) of sample PPY4, while the uptake of the compactivated MPPY4 sample remains unchanged (Supporting Figure

S11). Compaction, therefore, generates densified carbons that retain a high gravimetric hydrogen uptake compared to conventionally activated carbons.

Figure 4. Effect of densification on porosity of activated and compacted carbons; (a, c) nitrogen sorption isotherms and (b, d) corresponding pore size distribution (PSD) curves of polypyrrole-derived (a, b) compacted carbon (MPPY4) and (c, d) activated carbon (PPY4) prepared at 800 °C and KOH/PPy ratio of 4 before and after densification at 370 MPa (C5) and 740 MPa (C10). The PSD curves of the C5 and non-densified carbons are offset (y-axis) by 0.1 and 0.2 cm³ g⁻¹, respectively.

Table 3. Textural properties and hydrogen uptake of activated (PPY4) and compactivated (MPPY4) carbons before and after densification.

Sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (Å) ^a	H ₂ uptake at 20 bar (wt%) ^b	
				Excess	Total
PPY4	3225	2.43	13/34	5.0	6.5
PPY4-C5	2754	1.89	12/31	4.8	6.0
PPY4-C10	2060	1.30	12/28	4.6	5.9
MPPY4	3844	2.89	13/34	5.5	7.3
MPPY4-C5	3351	2.56	12/31	5.6	7.3
MPPY4-C10	3174	2.09	12/28	5.4	7.2

^aMaxima of pore size distribution obtained using non-local density functional theory (NLDFT) analysis. ^bExcess or total hydrogen uptake capacity at -196 °C and 20 bar.

3.2.2. High pressure hydrogen storage

The hydrogen uptake data discussed above was measured on a Hiden IGA, which has a maximum operating pressure of 20 bar. To determine the upper limits of hydrogen storage in compactivated carbons we assessed a second batch of the best performing samples (MPPY4 and MPPY4-C10) at higher pressure (up to 150 bar) using a Hiden Xemis analyser. There was very good agreement between IGA and Xemis hydrogen uptake data at -196 °C and pressure of up to 20 bar (Supporting Figure S12), which attests to the veracity of hydrogen uptake data obtained on the high pressure Xemis [22]. Figure 5 shows the high pressure (up to 150 bar) hydrogen storage capacity at -196 °C; the excess hydrogen uptake reaches a maximum of 6.5 wt% and 6.0 wt% for MPPY4 and MPPY4-C10, respectively at pressure of ca. 40 bar. This translates to total hydrogen storage of 9.6 wt% and 9.3 wt% for MPPY4 and MPPY4-C10, respectively (Supporting Table S2). At pressure of 150 bar, the total hydrogen storage reaches 14.2 wt% and 13.9 wt% for MPPY4 and MPPY4-C10, respectively (Supporting Table

S2). The observed cryogenic hydrogen storage of 14.2 wt% for sample MPPY4 is at the very upper limit of what has been observed for porous carbons [5,6,9,16,21,24,27-30,40-42]. It is also remarkable that even the densified MPPY4-C10 sample achieves gravimetric uptake of 13.9 wt%. Such a high gravimetric uptake for a densified sample with enhanced packing density has excellent implication for volumetric uptake as discussed below.

Figure 5. Hydrogen uptake of compactivated carbons, at -196 °C, before and after densification; excess and total hydrogen uptake of polypyrrole-derived compactivated carbon prepared at 800 °C and KOH/PPy ratio of 4, before (MPPY4) and after (MPPY4-C10) densification at 740 MPa.

The cryogenic hydrogen uptake of the compactivated carbons compares favourably with that of the best performing high surface area MOFs (Supporting Table S3). Indeed, the uptake

of the compactivated carbons is higher than that of benchmark MOFs such as MOF-5 [43], MOF-177 [44] and NOTT-112 [31], and comparable to that of Nu-100 [45] and MOF-210 [46], which have much higher surface area are the current record holders for gravimetric hydrogen storage in porous materials under cryogenic conditions. Furthermore, the higher packing density of the compactivated and/or pelletized carbons, 0.39 g cm^{-3} and 0.52 g cm^{-3} for MPPY4 and MPPY4-C10, respectively, means that their volumetric hydrogen storage capacity is very attractive (Supporting Table S2 and S3). Based on their packing density, MOFs achieve excess volumetric hydrogen uptake of $9 - 18 \text{ g l}^{-1}$, while the compactivated carbons reach excess volumetric storage of 25.4 and 31.2 g l^{-1} for MPPY4 and MPPY4-C10, respectively. The total volumetric hydrogen storage (at 80 bar) is 46 and 60.3 g l^{-1} for MPPY4 and MPPY4-C10, respectively, compared to between 12 and 28.5 g l^{-1} for the best performing MOFs (Supporting Table S3). At 150 bar, the volumetric uptake of MPPY4 and MPPY4-C10 reach very high values of 55.4 g l^{-1} and 72.3 g l^{-1} , respectively. The volumetric uptake of the compactivated carbons is the highest reported so far and is only matched by that of densified zeolite templated carbons [24], and densified activated ZIF-templated carbons [47].

3.2.3. Room temperature hydrogen storage

The excess and total hydrogen uptake isotherms of samples MPPY4 and MPPY4-C10 at room temperature are shown in Figure 6. For sample MPPY4, the excess hydrogen uptake varies from $0.5 \text{ wt\%}$ at 20 bar to $1.6 \text{ wt\%}$ at 150 bar (Supporting Table S4). The corresponding excess hydrogen uptake for sample MPPY4-C10 is $0.3 \text{ wt\%}$ and $1.3 \text{ wt\%}$ at 20 and 150 bar , respectively (Supporting Table S4). An excess hydrogen storage capacity of $1.6 \text{ wt\%}$ at room temperature and 150 bar is the highest reported for any porous material under those conditions and exceeds that of the best performing state-of-the-art materials, namely, $1.3 \text{ wt\%}$ for activated CNT superstructures [29], $1.2 \text{ wt\%}$ for a ZTC [48], $1.3 \text{ wt\%}$ for a ZTC in a separate

study [49], and 1.0 wt% for activated carbon (KUA5) [28]. We performed in-house benchmarking of our IGA data by comparison with commercially available carbon AX21 (Supporting Figure S13); AX21 has an uptake of 0.32 wt% at 20 bar, (which is similar to what has been previously reported from volumetric measurements [50]), compared to 0.5 wt% for the compactivated MPPY4 sample. The agreement between our IGA obtained uptake value for sample AX21 and previously reported data [50] attests to the reliability of our room temperature hydrogen storage measurements.

Figure 6. Hydrogen uptake at 25 °C of compactivated carbons before and after densification; excess and total hydrogen uptake of polypyrrole-derived compactivated carbon prepared at 800 °C and KOH/PPy ratio of 4, before (MPPY4) and after (MPPY4-C10) densification at 740 MPa. The total hydrogen uptake is calculated using micropore volume calculated using the Dubinin-Radushkevich (D-R) equation applied to CO₂ adsorption data obtained at 0 °C.

In calculating the total hydrogen uptake at room temperature, we considered the following; (i) the possibility that due to thermal effects, it may not be possible to probe the smallest pores with nitrogen adsorption at -196 °C [51,52], and (ii) that at 25 °C, the hydrogen may mainly adsorb in micropores rather than in all the space (i.e., including mesopores) available. We therefore determined the micropore volume of samples MPPY4 and MPPY4-C10 using the Dubinin-Radushkevich (D-R) equation from CO₂ adsorption data obtained at 0 °C and 25 °C (Supporting Figure S14). The D-R micropore volume obtained from the CO₂ sorption at 0 °C is 1.97 cm³ g⁻¹ for sample MPPY4 and 1.50 cm³ g⁻¹ for sample MPPY4-C10. (For CO₂ sorption at 25 °C, the D-R micropore volume was slightly lower at 1.71 cm³ g⁻¹ for sample MPPY4 and 1.25 cm³ g⁻¹ for sample MPPY4-C10). We note that these D-R micropore volume values are comparable to what has previously been reported for commercially available high surface area carbon (MSC-30) [53]. Using the D-R micropore volume from CO₂ sorption at 0 °C, we estimated the total hydrogen uptake as the excess uptake plus hydrogen stored in micropores (Supporting Tables S4 and S5 and Supporting Figure S15). For sample MPPY4 the total hydrogen uptake is 0.8 wt% at 20 bar and reaches 3.6 wt% at 150 bar, while for sample MPPY4-C10 the corresponding values are 0.6 wt% and 3.4 wt% at 20 and 150 bar, respectively (Supporting Table S4), which are attractive in the context of what has been reported to date [28,29]. The corresponding room temperature total volumetric hydrogen storage capacity at 20 bar is 3.1 g l⁻¹ for both sample MPPY4 and MPPY4-C10, rising to 14.0 and 17.7 g l⁻¹ at 150 bar (Supporting Table S4), which as far as we know, exceeds that of the best known carbon (KUA5) and MOFs (Supporting Table S5). We also estimated, for comparison purposes, the total hydrogen stored as computed using total pore volume from nitrogen sorption analysis (Supporting Figure S15); for sample MPPY4 the uptake ranges from 0.9 wt% at 20 bar to 4.5 wt% at 150 bar, while for MPPY4-C10 the corresponding values are 0.7 wt% and 4.2 wt% at 20 and 150 bar, respectively (Supporting

Table S4). This corresponds to room temperature total volumetric hydrogen storage capacity at 20 bar of 3.5 and 3.6 g l⁻¹ for sample MPPY4 and MPPY4-C10, respectively, rising to 17.6 and 21.8 g l⁻¹ at 150 bar (Supporting Table S4).

Our data shows that a high surface area associated with micropore/small mesopores delivers a respectable excess hydrogen uptake, while a large pore volume translates to a high overall total storage capacity. Moreover, the densified nature of the compactivated carbons means that they have higher volumetric hydrogen uptake (excess or total) than current benchmark materials (Supporting Table S3 and S5). There are various methods via which the packing density of carbons (or other powdered porous materials) may be obtained; in this study, the packing density of *powder* samples was determined by pressing a given amount of carbon in a 1.3 cm die at pressure of 74 MPa for 5 min.⁹ Packing density (d_{carbon}) of *powder samples* may also be estimated from the skeletal density using the equation; $d_{\text{carbon}} = (1/\rho_s + V_T)^{-1}$, where ρ_s is skeletal density and V_T is total pore volume. This equation computes the achievable packing density for powder samples although for the present study the samples were pelletised/compacted, which increased the actual packing density. Based on a measured (using helium sorption at 0 °C) skeletal density of 2.1 - 2.2 g cm⁻³ [53], the estimated packing density for *powdered forms* of sample MPPY4 and MPPY4-C10 would be ca. 0.3 and 0.4 g cm⁻³, respectively. Such packing density would still deliver volumetric hydrogen uptake values that are higher than for any previously reported material, a finding which we ascribe to the combination of high surface area and pore volume of the compactivated carbons.

3.4. CO₂ storage: Lowly activated and compactivated carbons

Pore size is known to be the main factor in determining physisorption-based CO₂ uptake onto solid state materials under conditions that mimic post-combustion flue gas streams [18-

20,29,54,55]. It has been shown that pores of size 6 – 7 Å are the most efficient in CO₂ capture and storage under low pressure conditions (0.1 to 1 bar) [18-20,29,54,55]. However, in conventional activated carbons, such pores are usually accompanied by low surface area, which limits the amount of CO₂ that can be stored. Given the similar pore size of the lowly activated carbons prepared at 600 °C, i.e., compactivated sample MPPY2600 and the activated analogue (PPY2600), and the higher surface area of the former, we were encouraged to compare their CO₂ uptake. The CO₂ storage capacity was measured at 25 °C and pressure range of 0 to 20 bar; the uptake isotherms are shown in Figure 7, and the storage capacity at pressure of 0.15 bar, 1 bar and 20 bar is given in Table 2. The CO₂ uptake of the compactivated MPPY2600 sample is much higher; at pressure of 1 bar the uptake of activated sample PPY2600 is 3.4 mmol g⁻¹, which is comparable to what has previously been reported for similar materials [56], while the compactivated MPPY260 sample has much higher uptake of 5.5 mmol g⁻¹. At 0.15 bar, a pressure that is particularly relevant to CO₂ capture from post-combustion flue gas streams, the uptake of the compactivated MPPY2600 carbon is 2.1 mmol g⁻¹, which is much higher than the 1.3 mmol g⁻¹ for the conventionally activated PPY2600 sample. The remarkable increase in CO₂ uptake, of ca. 60%, at low pressure (0.15 and 1 bar) reflects the increase in surface area under virtually non-changing pore size. It is noteworthy that the room temperature CO₂ uptake of 2.1 mmol g⁻¹ and 5.5 mmol g⁻¹ at 0.15 and 1 bar, respectively, (Supporting Figure S16), observed for sample MPPY2600 are the highest reported so far for non-doped carbons [18-20,54-56].

Figure 7. CO₂ uptake isotherms at 25 °C and pressure range 0 – 20 bar for polypyrrole-derived compactivated carbon (MPPY2600) and conventionally activated (PPY2600) carbon prepared at 600 °C and KOH/PPY ratio of 2.

We also explored how the improvement in gravimetric CO₂ uptake translates to volumetric uptake, which is a necessary measure of the efficiency of any material given that for use under flue gas stream conditions, the adsorbent is packed into a column wherein the CO₂ uptake per given space (volume) occupied by the adsorbent (i.e. volumetric uptake) should be maximised. The volumetric CO₂ uptake of porous materials is related to their packing density, which though low for powdered forms of highly activated carbons, can reach high values for lowly activated and compacted carbons [57]. The packing density of PPY2600 and MPPY2600 samples was found to be 0.92 and 0.85 g cm⁻³, which is in line with previously reported values for activated carbons of similar surface area and pore volume [9,57]. The volumetric CO₂ uptake is shown in Figure 8 and the uptakes at various pressures are summarised in Table 4. The volumetric CO₂ uptake of the compactivated MPPY2600 sample is not only enhanced over that of the conventionally activated PPY2600 sample, but is also higher than for carbon monoliths (sample A1) and activated carbon monoliths (sample

A3-36), which were recently shown to outperform all other materials [57]. For example, at 0.15 bar, which pressure is considered relevant for post combustion CO₂ capture, sample MPPY2600 achieves volumetric CO₂ uptake of 79 g l⁻¹ compared to 52 g l⁻¹ for PPY2600, and 30 – 40 g l⁻¹ for carbon monoliths (sample A1) and activated carbon monoliths (sample A3-36) [57]. At 1 bar, sample MPPY2600 stores 206 g l⁻¹ compared to 136 g l⁻¹ for PPY2600, and 130 – 160 g l⁻¹ for carbon monoliths (sample A1) and activated carbon monoliths (sample A3-36) [57]. The high volumetric uptake of sample MPPY2600 is very attractive in the context of the fact that a high surface area metal organic framework (MOF210), based on a crystal density of 0.25 g cm⁻³, has CO₂ storage of 4 g l⁻¹ and 10 g l⁻¹ at 0.15 and 1 bar, respectively [46]. The superior volumetric CO₂ uptake of sample MPPY2600 is maintained over the pressure range 1 – 20 bar (Figure 8 and Table 4).

Figure 8. Volumetric CO₂ uptake at 25 °C for compactivated MPPY2600 and conventionally activated PPY2600, compared with benchmark carbon and metal organic framework (MOF) materials.

Table 4. Packing density and volumetric CO₂ uptake for polypyrrole-derived compactivated (MPPY2600) and conventionally activated (PPY2600) carbons. Uptake data for benchmark carbon and metal organic framework (MOF) materials is shown for comparison.

Sample	Packing density g/cm ³	Volumetric CO ₂ uptake (g/l)				
		0.15 bar	1 bar	5 bar	10 bar	18 bar
PPY2600	0.92	52	136	251	286	341
MPPY2600	0.85	79	206	367	436	485
Carbon A1 ^a	1.00 ^a	38	157	278	316	335
Carbon A3-36 ^a	0.87 ^a	27	128	302	382	426
MOF210 ^b	0.25 ^c	4	10	38	73	152

^aData from reference 57. ^bData from reference 46. ^cCrystal density of MOF210.

4. Summary

A so-called compactivation route, which incorporates a mechanical compression step before thermochemical activation, generates carbons with porosity that is higher than analogous conventionally activated carbons but without significant changes in the pore size or pore size distribution. The compactivation process involves mechanical compression of powdered mixtures of KOH (activating agent) and carbon precursor (polypyrrole or biomass hydrochar) at 740 MPa into pellets/disks prior to thermochemical treatment at 600 °C (low levels of activation) or 800 °C (high levels of activation). The benefits of compactivation over conventional activation are such that lower quantities of activating agent (KOH) are required to achieve any given level of activation and porosity, which translates to a more efficient (and cheaper) use of the activating reagent. The method works for both highly activated and lowly activated carbons. For highly compactivated carbons (thermochemical activation at 800 °C), enhanced porosity (surface area and pore volume close to 4000 m² g⁻¹ and 3.0 cm³ g⁻¹, respectively) is achieved along with superior hydrogen uptake of up to 7.3 wt% (at -196°C

and 20 bar), rising to 9.6 wt% at 40 bar and 14.2 wt% at 150 bar. These gravimetric hydrogen uptakes translate to attractive cryogenic volumetric uptake of 38 g l⁻¹ at 40 bar, 46 g l⁻¹ at 80 bar and up to 56 g l⁻¹ at 150 bar. On densification, the highly compactivated carbons retain a much greater proportion of their porosity (surface area of 3200 – 3500 m² g⁻¹ and pore volume of 2.0 – 2.7 cm³ g⁻¹) whilst attaining high packing density, which means that they exhibit attractive volumetric hydrogen storage; 49 g l⁻¹ at 40 bar, 60 g l⁻¹ at 80 bar and up to 72 g l⁻¹ at 150 bar. The room temperature hydrogen storage of compactivated carbons, at 150 bar, reaches 3.4 wt% (14 g l⁻¹), while after densification it is 3.2 wt% (18 g l⁻¹). For lowly activated carbons (thermochemical activation at 600 °C), compactivation yields carbons with 35% higher surface area and pore volume with no change in pore size, which maintained at ca. 6.0 Å. The increase in surface area arising from such small micropores results in a significant increase in CO₂ storage capacity at 25 °C and low pressure ($\leq$ 1 bar); the uptake capacity rises from 1.3 to 2.1 mmol g⁻¹ at 0.15 bar, and from 3.4 to 5.5 mmol g⁻¹ at 1 bar. Also, due to their lowly activated nature, the compactivated samples have high packing density and therefore exhibit excellent volumetric CO₂ uptake of 79 g l⁻¹ and 206 g l⁻¹ at 0.15 and 1 bar, respectively (compared to 52 g l⁻¹ and 136 g l⁻¹ for conventionally activated analogue). Such volumetric CO₂ uptake is higher than for any material reported to date. Compactivation, therefore, generates carbons with high gravimetric and volumetric hydrogen and CO₂ uptake compared to conventionally activated carbons.

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Additional Information

Supporting information accompanying this paper is available.

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Supporting Information

Compaction: A mechanochemical approach to carbons with superior porosity and exceptional performance for hydrogen and CO₂ storage

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Excess and total hydrogen uptake

Our measurements provided the excess hydrogen uptake, which is the amount of hydrogen adsorbed in the carbons above that which would have been stored in the pores under similar conditions (temperature and pressure) assuming that there is zero energy of interaction between the hydrogen and the carbon pore walls. The total uptake is calculated from the excess storage by taking into account the amount of hydrogen compressed into the carbon pore volume space. Our gravimetric methods measured the excess hydrogen uptake (θ_{Exc}) from which the total storage (θ_T) was calculated from the equation:

$$\theta_T = \theta_{Exc} + \frac{100 \times d_{H_2} \times V_T}{(1 + d_{H_2} \times V_T)}$$

Where;

θ_T = total hydrogen uptake (wt%)

θ_{Exc} = excess hydrogen uptake (wt%)

d_{H_2} = density (g cm^{-3}) of compressed hydrogen gas at the relevant temperature and pressure.

The density was obtained from the National Institute of Standards and Technology (NIST) website (<http://www.nist.gov/>)

V_T = Pore volume ($\text{cm}^3 \text{ g}^{-1}$) of the carbon from nitrogen or CO_2 sorption analysis

The excess volumetric uptake capacity ($v\theta_{Exc}$), in g l^{-1} , was obtained using the equation;

$$v\theta_{Exc} = \theta_{Exc} \times d_{\text{carbon}}$$

where, d_{carbon} = packing density of the carbon

The total volumetric uptake capacity ($v\theta_T$), in g l^{-1} , was obtained using the equation;

$$v\theta_T = \theta_T \times d_{\text{carbon}}$$

Where, d_{carbon} = packing density of the carbon

The packing density of powder samples was determined by pressing a given amount of carbon in a 1.3 cm die at pressure of 7 MPa for 5 min. Alternatively relatively similar if slightly lower values (due to not taking into account the effects of compaction), can be obtained using the general equation; $d_{\text{carbon}} = (1/\rho_s + V_T)^{-1}$, where ρ_s is skeletal density and V_T is total pore volume.

Table S1. Carbon yield of polypyrrole-derived activated and compactivated carbons. (The yield depended on how carefully the washing step was performed to avoid losing sample matter. The yield generally varied to within $\pm 8\%$ such that, for example for PPY2 it is $22 \pm 1.8\%$ or for PPY4 it is $15 \pm 1.2\%$)

Sample	Yield (wt%)
PPY2	22
MPPY2	23
PPY3	19
MPPY3	18
PPY4	15
MPPY4	14

Table S2. Total gravimetric and volumetric hydrogen uptake at -196 °C of a compactivated carbon sample MPPY4 and after densification at 740 MPa (MPPY4-C10). Packing density of MPPY4 and MPPY4-C10 is 0.39 g cm⁻³ and 0.52 g cm⁻³, respectively.

Pressure (bar)	Hydrogen uptake			
	<u>Gravimetric (wt%)</u>		<u>Volumetric (g l⁻¹)</u>	
	MPPY4	MPPY4-C10	MPPY4	MPPY4-C10
40	9.6	9.3	37.4	48.4
50	10.3	10.0	40.2	52.0
60	10.9	10.6	42.5	55.1
70	11.4	11.2	44.5	58.2
80	11.8	11.6	46.0	60.3
90	12.2	12.1	47.6	62.9
100	12.7	12.5	49.5	65.0
110	12.9	12.8	50.3	66.6
120	13.2	13.0	51.5	67.6
130	13.4	13.3	52.3	69.2
140	13.9	13.7	54.2	71.2
150	14.2	13.9	55.4	72.3

Table S3. Surface area, pore volume hydrogen storage (at -196 °C) for compactivated carbons compared to the best benchmark metal organic frameworks (MOFs).

Sample	Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Gravimetric H ₂ uptake (wt%)		Volumetric H ₂ uptake (g l ⁻¹)		Reference
			Excess	Total ^a	Excess	Total ^a	
MPPY4 ^b	3596	2.56	6.5 ^c	11.8 (14.2) ^d	25.4	46.0 (55.4) ^d	This work
MPPY4-C10 ^b	3511	2.63	6.0 ^c	11.6 (13.9) ^d	31.2	60.3 (72.3) ^d	This work
MOF-5 ^e	3800	1.55	7.1	9.6 (11.1) ^d	9.2	12.5 (14.4) ^d	1
MOF-5 pellets ^f	2716	1.35	5.8	9.2	18.0	28.5	2,3
MOF-177 ^g	4740	1.89	7.3	11.3	15.3	23.7	4
NOTT-112 ^h	3800	1.62	7.6	10.0	17.5	23.0	5
NU-100 ^h	6143	2.82	9.95	16.4	14.9	24.6	6
MOF-210 ^h	6240	3.60	8.6	17.6	9.5	19.4	7

^aTotal H₂ uptake at -196 °C and 80 bar. ^bBatch 2 samples. ^cMaximum excess uptake is at ca. 40 bar.

^dValues in parenthesis are total H₂ uptake at 150 bar. Packing density values (g cm⁻³) used are: ^e0.13 (MOF-5)^{2,3}, ^f0.31 (MOF-5 pellets)^{2,3}, ^g0.21 (MOF-177)^{8,9}, ^h0.23 (NOTT-112), 0.15 (NU-100) and 0.11 (MOF-210)¹⁰

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Table S4. Excess and total gravimetric and total volumetric hydrogen uptake at room temperature (25 °C) of a compactivated carbon sample (MPPY4) and after densification at 740 MPa (MPPY4-C10). Packing density of MPPY4 and MPPY4-C10 is 0.39 g cm⁻³ and 0.52 g cm⁻³, respectively. (Values in parenthesis are computed using micropore volume calculated using the Dubinin-Radushkevich (D-R) equation applied to CO₂ adsorption data obtained at 0 °C).

Pressure (bar)	Gravimetric uptake				Total volumetric uptake (g l ⁻¹)	
	MPPY4		MPPY4-C10		MPPY4	MPPY4-C10
	Excess	Total	Excess	Total		
20	0.50	0.9 (0.8)	0.31	0.7 (0.6)	3.5 (3.1)	3.6 (3.1)
30	0.62	1.2 (1.1)	0.41	1.0 (0.9)	4.7 (4.3)	5.4 (4.7)
40	0.74	1.6 (1.3)	0.51	1.3 (1.1)	6.2 (5.1)	7.0 (5.7)
50	0.88	1.9 (1.6)	0.60	1.6 (1.3)	7.4 (6.2)	8.5 (6.8)
60	0.93	2.1 (1.8)	0.67	1.9 (1.6)	8.2 (7.0)	9.8 (8.3)
70	1.05	2.4 (2.0)	0.75	2.2 (1.8)	9.4 (7.8)	11.4 (9.4)
80	1.14	2.7 (2.3)	0.82	2.4 (2.0)	10.5 (9.0)	12.6 (10.4)
90	1.22	3.0 (2.5)	0.88	2.7 (2.2)	11.7 (9.8)	14.0 (11.4)
100	1.25	3.2 (2.6)	0.94	2.9 (2.4)	12.5 (10.1)	15.1 (12.5)
110	1.33	3.4 (2.8)	0.99	3.2 (2.6)	13.3 (10.9)	16.6 (13.5)
120	1.41	3.7 (3.0)	1.05	3.4 (2.8)	14.4 (11.7)	17.7 (14.6)
130	1.48	3.9 (3.2)	1.09	3.6 (3.0)	15.2 (12.5)	18.7 (15.6)
140	1.55	4.2 (3.4)	1.29	4.0 (3.2)	16.4 (13.3)	20.8 (16.6)
150	1.60	4.5 (3.6)	1.33	4.2 (3.4)	17.6 (14.0)	21.8 (17.7)

Table S5. Surface area, pore volume hydrogen storage at room temperature (25 °C) for compactivated carbons compared to benchmark carbon and metal organic frameworks (MOFs).

Sample	Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Gravimetric H ₂ uptake (wt%)		Volumetric H ₂ uptake (g l ⁻¹)		Reference
			Excess	Total ^a	Excess	Total ^a	
MPPY4 ^b	3596	2.56	1.60	4.5 (3.6) ^c	6.3	17.6 (14.0) ^c	This work
MPPY4-C10 ^b	3511	2.63	1.32	4.2 (3.4) ^c	6.9	21.8 (17.7) ^c	This work
Carbon KUA5 ^d	3183	1.25	1.00	2.7	5.1	13.7	1,2
ZTC	3800	1.70	1.30	2.9			3
ZTC	3600	1.66	1.30	2.8			4
MOF-5 ^e	3800	1.55	0.70	2.1	0.9 (2.2) ^f	2.7 (6.5) ^f	5
MOF-210 ^g	6240	3.60	0.50 ^h	2.7 ^h	0.6	3.0	6,7

^aTotal H₂ uptake at 25 °C and 150 bar. ^bBatch 2 samples. ^cValues in parenthesis are computed using micropore volume calculated using the Dubinin-Radushkevich (D-R) equation applied to CO₂ adsorption data obtained at 0 °C. The packing density values (g cm⁻³) used are: ^d0.50 (KUA5)^{1,2}, ^e0.13 (MOF-5)^{8,9}, ^f0.31 (assume MOF-5 pellet density)^{8,9}, and ^g0.11 (MOF-210)¹⁰. ^hUptake at 80 bar.

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Figure S1. Wide pore size distribution obtained using the non-local density functional theory (NLDFT) model for compactivated and activated carbons derived from polypyrrole (a – c) and wood sawdust (d); (a) PPY2 and MPPY2, (b) PPY3 and MPPY3, (c) PPY4 and MPPY4, and (d) S400 and S400P. The pore size distribution in the mesopore and macropore ranges shows that compactivation has no effect on these larger pores up to at least 2000 $\text{\AA}$.

Figure S2. Effect of KOH/PPy ratio on porosity of PPy-derived activated (PPY_x) and compactivated (MPPY_x) carbons; (a) and (c) show nitrogen sorption isotherms. (b) and (d) show pore size distribution curves obtained using the non-local density functional theory (NLDFT) model. (a) and (b) are for compactivated carbons, and (c) and (d) for activated carbons.

Figure S3. (A) Nitrogen sorption isotherms, and (B) pore size distribution curves of activated (PPY4) and compactivated (MPPY4) samples compared to commercially available high surface area activated carbon, AX21.

Figure S4. Powder XRD patterns of PPY-derived activated (PPY4) and compactivated (MPPY4) carbons. The XRD patterns of these compactivated and activated carbons, which exhibit the highest surface area are rather featureless. This suggests that the carbons are largely amorphous; a graphitic (002) peak normally present at 2θ of $22 - 26^\circ$ is hardly observed for both samples meaning that there is a dearth of adjacent graphite layers. A very broad and low intensity peak at ca. 44° is observed for both samples, which is the (100) peak for in-plane ordering of graphitic layers. The relative intensities suggest a slightly higher level of ‘graphitisation’ for the activated carbon PPY4 compared to the MPPY4 compactivated carbon.

Figure S5. Raman spectra of PPY-derived activated (PPY4) and compactivated (MPPY4) carbons. The broad bands at 1370 cm⁻¹ and 1595 cm⁻¹ may be ascribed to the so-called D-peak (for disordered carbon) and the G-peak (for graphitic carbons), respectively. The ratio of peak intensity (i.e., area) of the D-peak to G-peak (I_D/I_G) is ~ 1.4 for PPY4 and 1.5 for MPPY4 and thus marginally higher for MPPY4, which suggests a slightly lower level of graphitisation for the compactivated sample. This is in agreement with the powder XRD patterns in Figure S6.

Figure S6. TEM images of PPY-derived activated (PPY4) and compactivated (MPPY4) carbons. The compactivated and activated carbons show similar levels of disorder.

Figure S7. t-plot analysis curves for determining microporosity from nitrogen sorption data for samples S4800 and S4800P. The micropore surface area is as follows: S4800 (1157 m²/g) and S4800P (1413 m²/g).

Figure S8. Wide pore size distribution obtained using the non-local density functional theory (NLDFT) model for polypyrrole-derived compactivated carbon (MPPY2600) and conventionally activated (PPY2600) carbon prepared at 600 °C and KOH/PPY ratio of 2. The pore size distribution in the mesopore and macropore ranges shows that compactivation has no effect on these larger pores up to at least 800 Å.

Figure S9. Excess and total hydrogen uptake, at -196 °C, of polypyrrole-derived activated (PPY4) and compactivated (MPPY4) carbons prepared 800 °C and KOH/PPy ratio of 4 compared with the uptake of commercially available high surface area activated carbon (AX21).

Figure S10. (A) Excess hydrogen and deuterium hydrogen uptake of sample MPPY4, and (B) variation of the molar ratio of amount of deuterium (nD_2) and hydrogen (nH_2) adsorbed with pressure for sample MPPY4.

Figure S11. Effect of densification on hydrogen uptake of activated and compactivated carbons. Excess and total hydrogen uptake of polypyrrole-derived activated (PPY4) and compactivated (MPPY4) carbons prepared at 800 °C and KOH/PPy ratio of 4, before and after (C10) densification at 740 MPa.

Figure S12. Agreement between hydrogen uptake data from IGA or Xemis analysers. Excess hydrogen uptake data for sample MPPY4-C10 obtained at -196 °C on a Hiden IGA compared to that obtained on a Hiden Xemis analyser. The data from the two instruments, in the range 0 – 20 bar, is virtually identical.

Figure S13. Excess hydrogen uptake, at 25 °C, of polypyrrole-derived compactivated carbon before (MPPY4) and after densification at 740 MPa (10MPPY4) compared with the uptake of commercially available high surface area activated carbon (AX21).

Figure S14. CO₂ adsorption isotherms for samples MPPY and MPPY-C10 at pressure of up to 20 bar, which is equivalent to relative pressure (P/P_0) of ~ 0.57 at 0 °C and 0.33 at 25 °C.

Supporting Figure S15. Hydrogen uptake of compactivated carbons, at 25 °C, before and after densification; excess and total hydrogen uptake of polypyrrole-derived compactivated carbon prepared at 800 °C and KOH/PPy ratio of 4, before (MPPY4) and after (MPPY4-C10) densification at 740 MPa. The total hydrogen uptake is calculated by using either the total pore volume from nitrogen sorption at -196 °C or the micropore volume calculated using the Dubinin-Radushkevich (D-R) equation applied to CO₂ adsorption data obtained at 0 °C.

Figure S16. CO₂ uptake isotherms at 25 °C and pressure range 0 – 1 bar for polypyrrole-derived compactivated carbon (MPPY2600) and conventionally activated (PPY2600) carbon prepared at 600 °C and KOH/PPY ratio of 2.