Importance of pore size in high-pressure hydrogen storage by porous carbons

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Development of high-capacity hydrogen-storage systems utilizing physisorption at high pressure and low temperature is hindered by poor understanding of the pore size/shape requirements for achieving the maximum hydrogen uptake. Tuning the carbon structure and pore size of carbide-derived carbons (CDCs) with high accuracy by using different starting carbides, chlorination temperatures and activation temperatures allows rational design of carbon materials with increased hydrogen-storage capacity. Systematic experimental investigation of a large number of CDCs with controlled pore size distributions and specific surface area (SSA) shows that pores larger than ~1.5 nm contribute little to hydrogen storage. It has been experimentally demonstrated that, just as at ambient pressure, pores of 0.6–0.7 nm in diameter provide the largest H2 uptake per unit SSA at elevated pressures and liquid nitrogen temperatures. The effect of pore size was stronger than the effect of surface chemistry on the hydrogen uptake.

1. Introduction

The success of any future hydrogen economy depends on our ability to develop inexpensive materials with sufficient hydrogen-storage capacity [1,2]. Porous and high-SSA nanostructured carbons are among the major candidates due to their low density and (in most cases) inexpensive precursors [3–6]. High hydrogen uptake has been reported for templated carbons [7,8], but carbide-derived carbons (CDCs), produced by halogen leaching of crystalline carbides [9,10], offer the advantage of controlled average pore size and its distribution (PSD). Moreover, the pore shape and SSA of CDCs can be controlled by selection of precursor carbide and chlorination temperature [11–14]. This versatility allowed us to demonstrate that the previously accepted linear correlation between ambient pressure storage capacity and SSA (the “Chahine rule” [15]) is not generally valid, and that CDCs with narrow PSDs centered in the range 0.6–0.7 nm significantly outperform the linear mean [16]. This can be explained by the density of hydrogen physisorbed in subnanometer pores at 1 bar that is close to the density of liquid hydrogen [17].

Despite this new insight, storage capacities at 1 bar remain impractically low and a question remains whether the hydrogen uptake by carbon can be further increased by filling
larger pores at higher pressures. Therefore we extended our previous study to 60 bar, including data from 23-odd as-prepared CDCs based on different precursors, CDCs which have been purified and/or activated using physical or chemical treatments, and several activated carbons for comparison (see Tables 1 and 2). To the best of our knowledge, this represents the first summary of high-pressure storage results across a wide spectrum of porous carbons.

2. Experimental section

2.1. Carbon materials

CDC powders were produced by chlorination of TiC, SiC and Mo2C powders. Carbide powders were placed in a horizontal tube furnace and heated at temperatures between 400 °C and 1000 °C under chlorine gas flow (10–15 ml/min) for 3 h. CDC powders were then annealed at 600 °C for 2 h under hydrogen gas flow to remove residual chlorine and chloride trapped in pores [18]. After synthesis, chemical and physical activation has been performed on CDCs.

Chemical activation was performed on CDC using KOH reagent following the process described in detail in reference [19]. CDC carbons and KOH reagent have been mixed (ratio KOH/CDC 3/1 wt./wt.) and were heated to 750 °C. The KOH/CDC 3/1 wt./wt. ratio is typically used in commercial and experimental microporous activated carbons, such as AX21 which is known as one of the best carbons for hydrogen storage. For comparative purposes, some activated carbon materials have been prepared from anthracite or phenolic resin precursor using KOH/precursor ratios ranging from 1/1 to 3/1 using the experimental procedure described in [16].

2.2. Porosity characterization

The experimental setup and structure/composition of carbide powders for synthesis of CDCs have been described elsewhere [12]. Porosity analysis was carried out with Ar and N2 at liquid nitrogen temperature (77 K), and with CO2 at 273 K on samples outgassed for at least 12 h at 300 °C using a Quantachrome Autosorb-1. Argon sorption was conducted from relative pressure P/P0 of 10−6 to 1 to assess porosity and surface area data. Isotherms show increasing pore volume with increasing synthesis temperature. Isotherms of as-produced CDCs are type I, suggesting that CDCs are microporous according to the IUPAC classification. At 1000 °C chlorination temperature, there is a slight hysteresis showing a small amount of mesoporosity. Pore size distributions reported in Table 1 were correlated from Ar adsorption data using the nonlocal density functional theory (NLDFT) method for slit shaped pores provided by Quantachrome data reduction software version 1.2 and the SSA was calculated using the Brunauer–Emmett–Teller (BET) method.

Since the pore size distributions were very similar to the ones reported in our published papers [11–14] and the difference between pore size, pore volume and SSA was within several percent (close to the accuracy of measurements), we...

Table 1 – Pore characteristics and results of sorption measurements of non-activated and activated CDC derived from TiC.

<table>
<thead>
<tr>
<th>CDC synthesis conditions (precursor, chlorination temperature, treatment)</th>
<th>BET SSA [m²/g]</th>
<th>Pore volume [cm³/g]</th>
<th>Average pore size [nm]</th>
<th>Hydrogen uptake (77 K, 60 bar) [wt%]</th>
<th>Hydrogen uptake per SSA [10⁴ wt% g/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC, 400, H₂ ann</td>
<td>1143</td>
<td>0.5</td>
<td>0.65</td>
<td>3.3</td>
<td>2.78</td>
</tr>
<tr>
<td>TiC, 500, H₂ ann</td>
<td>1150</td>
<td>0.48</td>
<td>0.68</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>TiC, 600, H₂ ann</td>
<td>1247</td>
<td>0.53</td>
<td>0.73</td>
<td>3.1</td>
<td>2.72</td>
</tr>
<tr>
<td>TiC, 800, H₂ ann</td>
<td>1521</td>
<td>0.56</td>
<td>0.8</td>
<td>3.5</td>
<td>2.21</td>
</tr>
<tr>
<td>TiC, 1000, H₂ ann</td>
<td>1358</td>
<td>0.62</td>
<td>1.1</td>
<td>2.9</td>
<td>2.13</td>
</tr>
<tr>
<td>TiC, 400, KOH act</td>
<td>2228</td>
<td>0.9</td>
<td>1.2</td>
<td>4.5</td>
<td>2.06</td>
</tr>
<tr>
<td>TiC, 500, KOH act</td>
<td>1991</td>
<td>0.93</td>
<td>1.2</td>
<td>4.5</td>
<td>2.2</td>
</tr>
<tr>
<td>TiC, 600, KOH act</td>
<td>2307</td>
<td>0.95</td>
<td>1.1</td>
<td>4.2</td>
<td>2.0</td>
</tr>
<tr>
<td>TiC, 800, KOH act</td>
<td>2471</td>
<td>1</td>
<td>1.17</td>
<td>4.3</td>
<td>1.89</td>
</tr>
<tr>
<td>TiC, 1000, KOH act</td>
<td>1708</td>
<td>0.64</td>
<td>1.3</td>
<td>3.1</td>
<td>1.85</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 875 °C 2 h</td>
<td>1721</td>
<td>0.69</td>
<td>0.8</td>
<td>3.7</td>
<td>2.15</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 875 °C 6 h</td>
<td>2409</td>
<td>0.99</td>
<td>1.42</td>
<td>4.58</td>
<td>1.9</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 875 °C 8 h</td>
<td>2643</td>
<td>1.05</td>
<td>1.49</td>
<td>4.62</td>
<td>1.75</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 900 °C 2 h</td>
<td>1860</td>
<td>0.77</td>
<td>0.9</td>
<td>3.9</td>
<td>2.1</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 930 °C 2 h</td>
<td>2409</td>
<td>1</td>
<td>1.46</td>
<td>4.5</td>
<td>1.87</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 950 °C 2 h</td>
<td>3038</td>
<td>1.34</td>
<td>1.52</td>
<td>4.7</td>
<td>1.55</td>
</tr>
<tr>
<td>TiC, 600, CO₂ act 960 °C 1 h</td>
<td>2072</td>
<td>0.86</td>
<td>1.2</td>
<td>4.0</td>
<td>1.93</td>
</tr>
</tbody>
</table>
refer readers to the above references for more details. However, we would like to stress that the values included in Table 1 were measured on the same batches of CDC that were used for hydrogen storage in this work. This provides the highest accuracy and eliminates possibility that some uncontrolled deviations in the synthesis process may affect the data.

2.3. High-pressure H₂ uptake measurements

Hydrogen uptake was measured at liquid nitrogen temperature (77 K) by using a home-built Sieverts apparatus [21]. Gas is admitted from a dosing cell with known volume to the sample cell; the gas pressure and temperature are controlled and recorded. A unique feature is the use of 3 pressure gages covering 0–60 bar in overlapping ranges for increased accuracy. The Modified-Benedict-Webb-Rubin (MWBR) equation of state was used for analysis of results [22]. Excess adsorption isotherms were determined by measuring absolute adsorption up to 60 bar, and then subtracting the empty volume contribution using the calculated volume and known system volumes. Most experiments were performed with the sample at 77 K. In one experiment designed to measure the enthalpy of adsorption, the sample was located in a cryostat allowing measurement of 5 hydrogen isotherms between 30 K and 300 K [21]. One of the samples was also annealed to temperatures up to 800 °C to determine whether physisorbed species or surface functionalities affect hydrogen uptake.

3. Results and discussion

The pore characteristics measured under N₂ and CO₂ sorption as well as the results of H₂ sorption measurements of the TiC-CDC samples before and after activation are listed in Table 1. The data obtained for CDCs produced from Mo₂C and SiC are detailed in Table 2.

![Fig. 1 – 77 K Sieverts isotherms for TiC-CDC chlorinated at 600 °C and CO₂-activated for various times at different temperatures.](image)

![Fig. 2 – PSDs for CDCs activated at different temperatures.](image)

![Fig. 3 – Excess gravimetric capacity vs. SSA results from a large data set of CDCs and other nanoporous carbons.](image)

Table 2 – Pore characteristics and results of sorption measurements of non-activated and activated CDC derived from Mo₂C and SiC.

<table>
<thead>
<tr>
<th>CDC synthesis conditions (precursor, chlorination temperature, treatment)</th>
<th>BET SSA [m²/g]</th>
<th>Pore volume [cm³/g]</th>
<th>Average pore size [nm]</th>
<th>Hydrogen uptake (77 K, 60 bar) [wt%]</th>
<th>Hydrogen uptake per SSA [10³ wt% g/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₂C, 400, H₂ ann</td>
<td>1481</td>
<td>0.65</td>
<td>0.9</td>
<td>2.63</td>
<td>1.89</td>
</tr>
<tr>
<td>Mo₂C, 600, H₂ ann</td>
<td>1980</td>
<td>1.05</td>
<td>1.06</td>
<td>4.0</td>
<td>2.02</td>
</tr>
<tr>
<td>Mo₂C, 660, H₂ ann</td>
<td>1875</td>
<td>1.14</td>
<td>1.1</td>
<td>4.35</td>
<td>2.32</td>
</tr>
<tr>
<td>Mo₂C, 800, H₂ ann</td>
<td>1298</td>
<td>1.08</td>
<td>1.25</td>
<td>3.6</td>
<td>2.3</td>
</tr>
<tr>
<td>SiC, d = 0.6 μm, 1000, H₂ ann</td>
<td>1178</td>
<td>0.54</td>
<td>1</td>
<td>3.1</td>
<td>2.63</td>
</tr>
<tr>
<td>SiC, d = 6 μm, 1000, H₂ ann</td>
<td>1155</td>
<td>0.48</td>
<td>0.8</td>
<td>3.07</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Mo₂C (400 °C) has the largest SSA (roughly, area under the curve) but a greater fraction corresponds to pores >1.5 nm diameter as compared to the 875 °C 8 h sample. While larger pores are less efficient than smaller pores, the two materials perform similarly because a smaller fraction of pores <1.5 nm in the sample activated at 950 °C is compensated by a larger total SSA resulting from activation at higher temperatures. Those results confirm the importance of small pores for high-pressure storage and are in agreement with the theoretical predictions of Bhatia and Myers [23] and experimental results obtained from templated carbons [24], revealing that the Chahine rule is not universal.

Fig. 3 reveals the highly scattered nature of capacity vs. SSA results from a large data set of CDCs and other nanoporous carbons. If details of the pore structure (size, shape etc.) were irrelevant, capacity would vary linearly with SSA. In fact, many traditional porous carbons, including the well-studied AX21, are found to obey the Chahine rule plotted as the black line in Fig. 3. Broadening the scope to include CDCs and some other state of the art porous carbons reveals a much more scattered result, with several materials outperforming the linear prediction and a few underperforming it. The blue and red dashed lines in Fig. 3 delineate approximately the best and worst material results obtained to date. Our detailed studies on the newer CDC materials indicate that materials outperforming the Chahine rule generally exhibit a greater...
fraction of pores <1.5 nm and/or a 0.7 nm median pore size in the respective PSDs. As at 1 bar (Fig. 1 in Ref. [17]), there is no general and universal linear correlation between storage capacity and total surface area, indicating that PSDs, average pore sizes, and possibly pore shape, play an important role.

A clear and direct dependence of storage capacity on pore size is obtained by plotting hydrogen storage normalized to SSA vs. pore size, as was done for 1 atm storage [16]. Fig. 4 shows the results. The smallest pores provide the greatest contribution to total capacity, since the overlap of the interaction potential fields from the interior pore surface will enhance the carbon–hydrogen interaction. Furthermore, materials with monodisperse smaller pores have higher SSA for a given pore volume. This means that hydrogen storage is dominated by small pores and thus not directly connected to total SSA. Even at high-pressure, H₂–H₂ interactions inside large pores are not strong enough for such pores to contribute significantly to overall capacity. Since storage occurs predominantly on the pore surfaces, the interior volume of large pores is essentially wasted and merely degrades the volumetric capacity. Our data and conclusions are completely borne out by a new calculation from Cabria et al. [25] who show that the optimum slit pore width remains well below 1 nm even for hydrogen pressures as high as 20 MPa (200 bar).

Post-treatment of CDC samples, such as activation or surface modification, will continue to be crucial in ongoing efforts to meet criteria for applications. We showed previously that significant gains are obtained by opening small pores by purifying in hydrogen to remove Cl₂ molecules trapped in nanopores during synthesis [18]. Though the overarching design criterion is to obtain large SSA with pores <1 nm, it is theoretically possible to obtain very high hydrogen uptake in carbon materials, perhaps even at temperatures near ambient, by controlling the pore surface chemistry to increase the heat of adsorption.

To better understand the energetics of adsorption, high-pressure hydrogen isotherms were collected as a function of temperature between 30 K and 300 K of TiC-CDC chlorinated at 800 °C with annealing in NH₃ at 600 °C (Fig. 5a-c). After ammonia treatment, the sample was annealed up to 800 °C under vacuum to remove the majority of the surface functionalities. This material does not show the highest hydrogen uptake, but it was selected to eliminate possible effects of chemical/structural changes caused by activation of CDC. At 30 K, TiC-CDC shows that the hydrogen uptake saturates around 5.5 wt% at pressures close to ambient. However, the saturation pressure increases with temperature. At room temperature, this CDC adsorbs less than 0.5 wt% at the maximum pressure and the saturation is not reached. The isosteric heat of adsorption was calculated as a function of hydrogen loading from the isotherms between 30 K and 300 K using the Clausius–Clapeyron equation,

$$Q_{st} = \frac{R}{M} \left( \frac{d}{d(1/T)} \ln P \right)_{N_{ads}} \tag{1}$$

The results of this calculation are shown in Fig. 5d. At low loading the isosteric heat reaches ~8.5 kJ/mol, decreasing to ~5.5 kJ/mol at high loadings, indicating that hydrogen begins

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**Fig. 2** – Pore size distributions from the two best-performing activated TiC-CDC materials in Fig. 1 (dotted and dashed lines), as well as their non-activated precursor (600 °C CDC, solid line).

**Fig. 3** – Excess capacity at 77 K, 60 bar vs. a) BET SSA (“Chahine” plot) and b) pore volume for a variety of CDCs and activated carbons (ACs).
to fill the lower energy binding sites. We measured the content of major impurities in the TiC-CDC sample using prompt gamma activation analysis (PGAA) [26] before and after vacuum annealing and determined that the hydrogen content was below 0.09%, chlorine below 0.04% and titanium content was 0.1% before and <0.015% after annealing. While the oxygen content cannot be measured by PGAA, we can conclude that we deal with a very pure carbon and the heat of adsorption values that we obtained can be considered as a physical constant for carbon with a given structure and pore size. The low-loading isosteric heat is nearly double that of hydrogen in MOF-5 (~4.8 kJ/mol) [21]. The heat of adsorption at low hydrogen loading does not change after annealing and only slightly increases in the 1–2.5 wt% range. These experiments show that surface chemistry has a secondary role compared to the pore size, since only a minor increase in hydrogen uptake occurs after heating to the temperature where most of the surface species are removed. Fig. 5 shows that the typical TiC-CDC has a higher heat of adsorption (above 8.5 kJ/mol) than AX-21 (6.5 kJ/mol) at low hydrogen loading, and just ~25% lower uptake at ~60% lower SSA. This again shows the importance of selecting the correct pore size and maximizing the volume of those pores in the material.

Fig. 4 – Excess capacity normalized to SSA vs. average pore size for the samples in Fig. 3.

Fig. 5 – Sieverts excess H₂ isotherms for TiC-CDC chlorinated at 800 °C measured at 33, 77, 87, 150 and 300 K, after outgassing at 200 °C (a), 600 °C (b) and 800 °C (c). Filled and open symbols correspond to adsorption and desorption, respectively. The isosteric heat of adsorption (d) was calculated using the Clausius–Clapeyron equation and H₂ isotherms measured between 30 K and 300 K.
4. Conclusions

In summary, nanoporous carbons with tunable pore size and specific surface area up to 3000 m²/g available for hydrogen storage have demonstrated a gravimetric hydrogen-storage density of 4.7 wt% at elevated pressure obtained either with TiC chlorinated at 600 °C activated under CO₂ or low temperature synthesized CDCs (400 or 500 °C) activated under KOH. While small pores (1 nm or below) are efficient for hydrogen sorption and lead to an increased heat of adsorption, mesopores do not contribute much to storage of hydrogen under these conditions. Annealing of samples has shown that the pore size effect is stronger than that of functional groups on the carbon surface. A higher SSA and larger pore volume increase the hydrogen uptake for a given pore size. Our findings provide guidance for optimal design of carbon materials for high-pressure hydrogen storage at cryogenic temperatures by realizing that a large volume of small open pores with narrow size distribution is the key to high hydrogen uptake.

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