

## Tailoring of Nanoscale Porosity in Carbide-Derived Carbons for Hydrogen Storage

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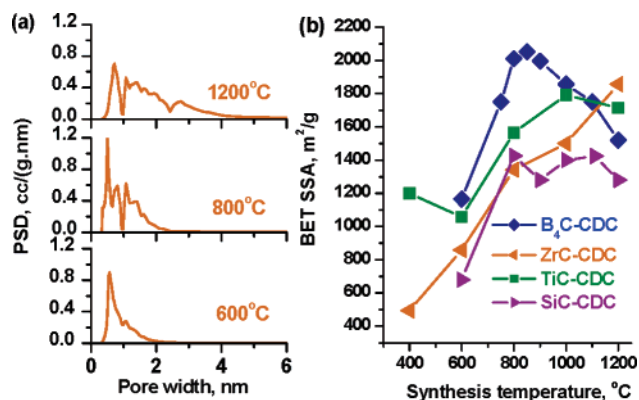
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The success of any future hydrogen economy depends on our ability to develop inexpensive materials with sufficient hydrogen-storage capacity.<sup>1</sup> Many types of materials have been tried, including carbon nanotubes (CNT),<sup>2</sup> activated carbons,<sup>3</sup> metal-organic framework compounds (MOF),<sup>4</sup> metal hydrides,<sup>5</sup> and clathrates.<sup>6</sup> Recent reviews<sup>7–9</sup> show that none of these currently meet the target. Carbon-based nanomaterials were among the major candidates due to their lightweight and abundant natural precursors,<sup>7,10</sup> but nanoscale and nanoporous carbons<sup>2,11</sup> (activated carbon, exfoliated graphite, fullerenes, nanotubes, nanofibers, and nanohorns) have not fulfilled their initial promise.

At the same time, a largely unknown class of porous carbons offers great potential for pore size control. Carbide-derived carbons (CDC) are produced by high-temperature chlorination of carbides. Metals and metalloids are removed as chlorides, leaving behind a collapsed noncrystalline carbon with up to 80% open pore volume. The first CDCs ca. 1920 were waste products from the production of chlorides from cheap and abundant carbides. The detailed nature of the porosity—average size and size distribution, shape, and total specific surface area (SSA)—can be tuned with high sensitivity by selection of precursor carbide (composition, lattice type)<sup>12–14</sup> and chlorination temperature.<sup>12</sup> The optimum temperature is bounded from below by thermodynamics and kinetics of chlorination reactions and from above by graphitization, which decreases SSA and introduces H<sub>2</sub>-sorbing surfaces with binding energies too low to be useful.

Hydrogen sorption in two CDC materials was studied several years ago and was found to be promising.<sup>15</sup> Here we report a systematic study of the effects of tailored porosity on the hydrogen sorption capacity. We synthesized a large number of CDC materials using different starting carbides (B<sub>4</sub>C,<sup>13</sup> ZrC,<sup>14</sup> TiC, and SiC<sup>16</sup>) and chlorination temperatures to explore the effect of variable pore size and volume (Supporting Information 1). Sorption experiments at 77 K and 1 atm H<sub>2</sub> (see Supporting Information for details) covered a wide range of average pore sizes (0.5–1.4 nm) and SSA (500–2000 m<sup>2</sup>/g). MOF-5, single- (SWCNT) and multi-walled carbon nanotubes (MWCNT) were included in our study for comparison.

Atomic-level porosity control in CDC is achieved by exploiting the robust host carbide lattice as a template, permitting controlled layer-by-layer metal extraction by optimizing the chlorination parameters. CDCs have unique features which make them attractive candidates for hydrogen storage: (1) narrow pore size distribution tunable with better than 0.05 nm sensitivity in the range ~0.5 to ~1.5 nm;<sup>12</sup> (2) SSA up to 2000 m<sup>2</sup>/g;<sup>13</sup> (3) up to ~80% open pore



**Figure 1.** Typical pore size distributions (PSD) of ZrC-CDC produced at different chlorination temperatures (a) and SSA of CDC from four different carbides as a function of temperature (b).

volume available to hydrogen (no closed porosity); and (4) moderate cost—just a fraction of that of CNT and close to that of synthetic activated carbons. Unlike activated carbons produced from organic precursors,<sup>17</sup> there is no hydrogen in the CDC structure. If necessary, residual chlorine and chlorides trapped in pores can be removed by annealing in hydrogen. The pore size distributions for ZrC-CDC broaden and shift to larger size with increasing chlorination temperature (Figure 1a). This is accompanied by an initial increase in SSA (Figure 1b), but only to a certain point above which graphitization leads to elimination of small pores and growth of larger pores (compare the curves for 600 and 1200 °C in Figure 1a).

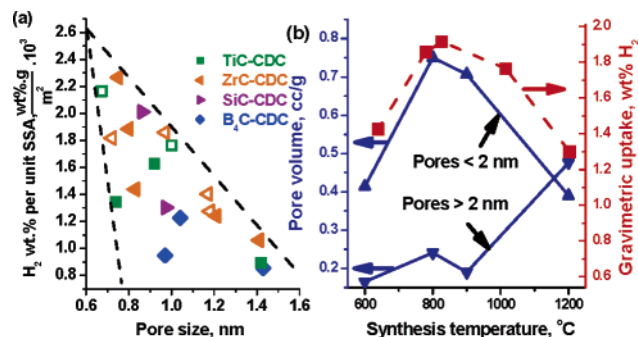
Traditionally, hydrogen sorption data are plotted as a function of SSA, and a linear dependence is expected.<sup>11,18,19</sup> Thus, we should observe the highest hydrogen sorption for the CDC with the highest SSA, namely, B<sub>4</sub>C-CDC produced at 800 °C. However, this material shows a value of 1.91 wt % of hydrogen compared to 2.55 wt % for TiC-CDC produced at the same temperature and having a lower SSA (Figure 1b). Careful analysis of the pore size and volume shows that the traditional way of plotting may be misleading. While both gravimetric and volumetric density show increasing sorption with SSA, capacities are scattered more than 100% among materials with the same SSA. It is natural to expect that other factors, such as the size and shape of pores, surface termination, and carbon structure, may affect the physisorption of hydrogen molecules. Therefore, we replotted the sorption data in a different way.

A clear dependence on pore size is seen when hydrogen storage normalized to SSA is plotted as a function of pore size (Figure 2a). The smallest pores provide the highest capacity, while the contribution from larger ones is marginal. Furthermore, materials

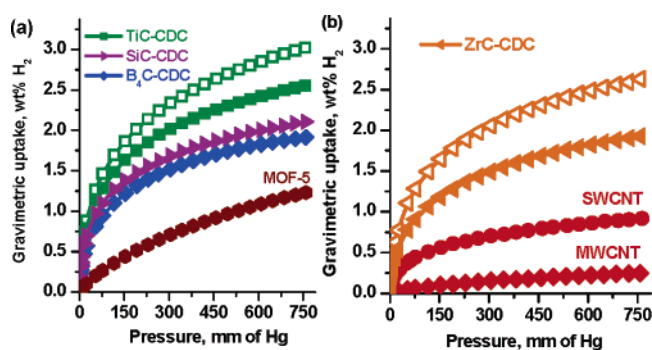
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**Figure 2.** Effect of pore size on hydrogen sorption. (a) Hydrogen storage normalized to surface area plotted as a function of pore size for several CDCs. The general trend defined by the dashed line envelopes indicates that small pores are more efficient than large ones for a given SSA. Solid symbols stand for as-produced and empty for hydrogen-annealed CDC. (b) Pore volume for micropores (<2 nm) and mesopores (>2 nm) in comparison with the gravimetric hydrogen uptake as a function of chlorination temperature for B<sub>4</sub>C-CDC.



**Figure 3.** Hydrogen sorption isotherms. CDC produced from different carbides compared to MOF-5 (a) and nanotubes (b). Solid symbols stand for as-produced and empty for hydrogen-annealed CDC. All isotherms are completely reversible, with no hysteresis.

with smaller pores will have higher SSA for a given pore volume, thus, in agreement with computer simulation work performed on microporous carbon<sup>20</sup> and carbon nanotubes.<sup>20,21</sup> Hydrogen storage is dominated by small pores, and thus not directly connected to total SSA. Figure 2b shows a clear correlation between micropore volume and capacity in B<sub>4</sub>C-CDC. Increasing the volume of pores with diameters greater than 2 nm is accompanied by a decrease in capacity. This is consistent with the previously observed dense hydrogen adsorption in subnanometer pores.<sup>22</sup>

Post-treatment of CDC samples, such as activation or surface modification, offers additional potential for controlled tuning of storage capacity. Annealing in hydrogen removes Cl<sub>2</sub> trapped during synthesis, opening small pores and leading to increased SSA, pore volume, and H<sub>2</sub> capacity. Enhancements up to 75% were obtained in this manner, leading to 3.0 wt % for annealed TiC-CDC (Figure 3). Prompt  $\gamma$ -ray activation analysis (PGAA)<sup>23</sup> gave an upper limit of one H per 500 carbons, confirming that the cleaning mechanism is Cl<sub>2</sub> removal and not H termination of pore surfaces.

CDCs have demonstrated a higher volumetric and gravimetric storage capacity compared to MOF-5 (Figure 3a), SWCNT,<sup>2</sup> and MWCNT (Figure 3b). Sievert's experiments conducted in parallel at NIST confirm the sorption results described here and demonstrate that gravimetric hydrogen uptake by CDCs is about twice that of

MOF-5 and several times higher than that of HiPco or chemically modified SWCNT.<sup>2</sup> Considering that only about 30% of the total CDC pore volume accessible to argon is currently used by hydrogen at ambient pressure, there is a large potential for increased capacity at modestly elevated pressure.

We have demonstrated that nanoporous CDCs with tunable pore size, specific surface area up to 2000 m<sup>2</sup>/g, and pore volume up to 1 cm<sup>3</sup>/g available for hydrogen storage possess gravimetric hydrogen storage density up to 3.0 wt % at 1 atm pressure and 77 K. Small pores (1 nm or below) are most efficient for hydrogen sorption, while mesopores detract from volumetric capacity and contribute little to gravimetric capacity. Large SSA and total pore volume increase hydrogen uptake for a given pore size. This study supports theoretical predictions by showing that a large volume of small open pores with narrow size distribution is the key to high hydrogen uptake.

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**Supporting Information Available:** Experimental details, synthesis conditions, and results of sorption experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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