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Enhanced volumetric hydrogen and methane storage capacity of monolithic carbide-derived carbon

Sun-Hwa Yeon [a], Isabel Knoke [a], Yury Gogotsi [a,*], John E. Fischer [b]

[a] Department of Materials Science and Engineering and A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, PA 19104, USA
[b] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

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ABSTRACT

Carbon-based cryosorbers are generally synthesized in the form of powders, which compromises the volumetric capacity in gas storage applications. Here we report the synthesis of monolithic carbide-derived carbon (CDC) by chlorination of fully-dense ceramic titanium carbide plates. Volume change is minimal, consistent with conformal transformation from TiC to CDC, and the weight loss is consistent with nearly 100% conversion. The resulting materials have a microporous carbon structure with little or no macroporosity and exhibit enhanced volumetric gas storage capacity compared to powder equivalents. Optimized volume uptakes are 35 g L^{-1} at −196 °C and 60 bar for H_2, 193 V(STP) v^{-1} at 35 bar and 219 V(STP) v^{-1} at 60 bar (25 °C) for CH_4. Monolithic CDCs thus offer potential as gas storage media for on-board fuel-cells and other applications.

1. Introduction

While safe on-board storage of gases such as H_2 or CH_4, having inherent clean burning characteristics, is of great interest for future transportation technology, the only options currently available are pressurization or liquification, respectively. Two classes of solid state materials, namely metal hydrides and high porosity adsorbents, can in principle provide better performance than high-pressure hydrogen storage tanks. To date, none of these technologies simultaneously meet practical criteria for gravimetric and volumetric capacity, cost, and safety.

On a volumetric basis, the best adsorbent for gas storage is a metal–organic framework (MOF) compound PCN-14 with 28% higher methane capacity than the DOE target [1]. This compound also outperforms activated carbons optimized for high specific surface area and micropore volumes [2–4]. Activated carbons derived from hardwood, coconut shell, or polymers, exhibit natural gas (methane) storage performance comparable to that of compressed natural gas at 250 bar [5], with remarkable volumetric methane uptakes up to ~200 V v^{-1} reported at 27 °C and 40 bar [6].

The standard procedure to test activated carbon (powder, granular, or fibers) is to measure gas volumes per storage material weight, which, however, leads to ambiguities in the conversion from gravimetric to volumetric capacities due to widely varying sorbent densities. The effort to develop gas storage systems led to pelletizing carbon adsorbents with or without a binder to minimize useless voids between the particles [7,8], but both the density and hardness were too low to enhance the volumetric gas storage capacity [8]. To overcome this problem, the use of bulk precursors has been attempted in the form of compressed cellulose pellets [9]. However, a long activation time (>19 h) was required to obtain a high Brunauer–Emett–Teller (BET) surface area of about 2000 m^2 g^{-1}, which also led to a low bulk density (0.56 g cm^{-3}) of the pelletized material due to the loss of carbon atoms. Another attempt to densify carbon structures involves sintering the powder under high pressure and temperature [10], which can adversely affect pore accessibility due to increased closed porosity and decreased sorption efficiency.

Carbide-derived carbon (CDC) possesses tunable pore structure, narrow pore size distribution in the range of 0.5–3 nm, and specific surface area (SSA) up to 3000 m^2 g^{-1} formed through selective etching of crystalline metal carbides [11–13]. Previous work with titanium carbide-derived carbon (TiC-CDC) activated with CO_2 and KOH [14] showed enhanced hydrogen and methane storage capacity due to distinct improvements in pore volume and a high specific surface area exceeding 3000 m^2 g^{-1}, but did not increase the practical density (packing density) of the post-activated CDCs obtained from the powder TiC precursor. Since small micropores (1 nm or smaller) are efficient for high-pressure physisorption of both H_2 [15] and CH_4 [14], macropores between the powder particles contribute little to the total gas storage. Sintered TiC ceramics, which can be manufactured as plates and films [16], can serve as an attractive alternative precursor for the preparation of carbon

* Corresponding author. Tel.: +1 215 895 6446; fax: +1 215 895 1934.
E-mail address: gogotsi@drexel.edu (Y. Gogotsi).

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plates with no macroporosity. However, only powders and films of CDC have been reported thus far [17–20]. In this work, we demonstrate significantly improved bulk density of TiC-CDCs by using a ceramic precursor, and producing TiC-CDC plates. This leads to enhanced volumetric capacity without the detrimental effects of pelletizing powder material.

2. Experimental

2.1. Sample preparation

To produce CDC plates, TiC sputtering targets (purity 99.5%) were purchased from Angström Scientific and cut to an appropriate size (usually 12 × 6 × 0.25 mm) using a diamond saw. Vendor-furnished impurity contents (ppm) were: Mg < 2, Al < 20, Si ~ 0.01, P < 0.01, Ca ~ 10, V < 2, Cr ~ 7, Mn < 1, Fe ~ 0.01, Ni ~ 3, Cu ~ 1, Cd < 5, and Pb < 2. The measured density 4.92 g cm^{-3} is the crystallographic value indicating full densification; the average grain size is 2 μm. TiC-CDCs were produced by chlorination of TiC plates. These were placed in a horizontal tube furnace, purged in flowing argon, heated to the target temperature (600–1200 °C) under flowing chlorine (10–15 cm^3 min^{-1}) for 3 h, then annealed at 600 °C for 2 h under flowing hydrogen to remove residual chlorine and titanium tetrachloride trapped in pores [17,21]. Sample transfer from the furnace to the measurement apparatus involved a brief exposure to air, so all measurements were preceded by a degassing procedure consisting of at least 20 h at 300 °C in 0.2 torr vacuum, which is sufficient, in our experience, to remove adsorbed water and CO_2. Further experiments, including mass measurement, were performed in a glove box with circulating argon. Integrity of the plates after conversion was sufficient to allow density measurement from their dimensions and mass.

2.2. High-pressure hydrogen and methane sorption measurement

Hydrogen and methane uptake experiments were performed on a custom-built volumetric Sieverts-type apparatus described in detail elsewhere [22]. The Modified-Benedict–Webb–Rubin (MBWR) equation of state was used for analysis of the results [23]. The empty cell volume was accurately measured at room temperature. Excess adsorption isotherms were determined by measuring the absolute adsorption up to 60 bar, and then subtracting the empty volume contribution using the calculated volume and known system volumes. The gravimetric storage capacity in wt.% is obtained from grams of gas per 100 g of carbon. Most experiments were performed with the sample at ambient temperature for methane uptake and at −196 °C for hydrogen uptake, respectively.

2.3. Low-pressure nitrogen sorption measurement

Gas adsorption analysis was performed using a Quadrasorb system (Quantachrome Instruments) with N_2 adsorbate at −196 °C, which is sensitive to pore sizes in the range ~0.5–50 nm. Pore-size distributions (PSDs) and pore volumes were determined using the quenched solid density functional theory (QSDFT) method provided by Quantachrome's data reduction software. The QSDFT model is devised for modeling adsorption in heterogeneous materials with corrugated amorphous walls and takes into account the effects of surface roughness and heterogeneity explicitly [24,25].

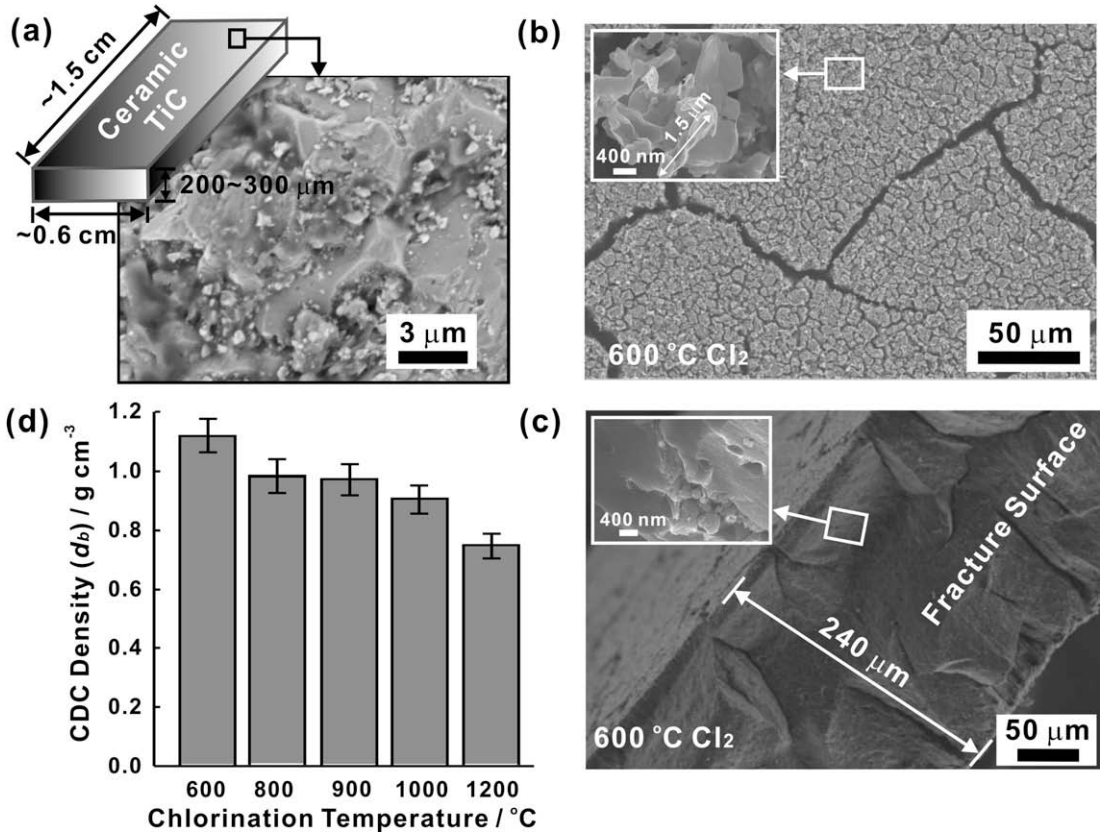

Fig. 1. Dimensions and SEM micrograph of the surface of a ceramic TiC plate (a). SEM micrographs of surface (b) and fracture surface (c) of TiC-CDC plates after chlorination and their bulk densities (d_b) (d). The insets show high resolution SEM images of the surface (b and c). Error bars in (d) are estimated from dimensional irregularities and mass loss during handling the plates. All TiC-CDCs were treated in Cl_2 at the indicated temperatures for 3 h and annealed in H_2 at 600 °C for 2 h.