

NANOPOROUS CARBIDE-DERIVED CARBONS (CDC) WITH TUNABLE PORE SIZE

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Introduction

Disordered porous carbons are potentially useful in many application areas. Supercapacitor electrodes benefit from high specific surface area. Porous carbon anode materials for Li-ion batteries exhibit relatively high rate capacity due in part to porosity. Water purification and filtration also rely on materials with high specific surface areas. For perm-selective membranes, control of pore size is also important. Perhaps the most demanding application is hydrogen storage for fuel cell powered transportation; here the porosity must be controlled in such a way that specificity, capacity and kinetics are simultaneously optimized.

A possible solution to this problem is high temperature gas phase halogenation of crystalline precursor carbides [1]. These can be binary or ternary compounds, or alloys. The basic notion is that removal of metals and metalloids (yielding halide byproducts) leaves behind an “amorphous” carbide with connected nanoscale pores. The size, shape and density of these pores depend on the choice of precursor crystal (constituents, lattice constant) and processing conditions, usually low pressure chlorination at temperatures from 300^o to 1200^o C.

Figure 1 shows a prototypical precursor, Ti₃SiC₃. The lattice is hexagonal, and there exist chains of Ti (red) and Si (blue) along the stacking direction. The chains are responsible for the *open* porosity exhibited by this material after chlorine treatment, for which the reaction is



The pore size distribution and total pore volume are controlled by details of chlorination reaction (temperature, pressure, time) and by crystal structure of precursor.

Results and Discussion

Aliquots of Ti₃SiC₃ powder were heated in flowing Cl₂ at temperatures from 200 to 1200^oC. Powder x-ray diffraction showed that the crystalline precursor was completely

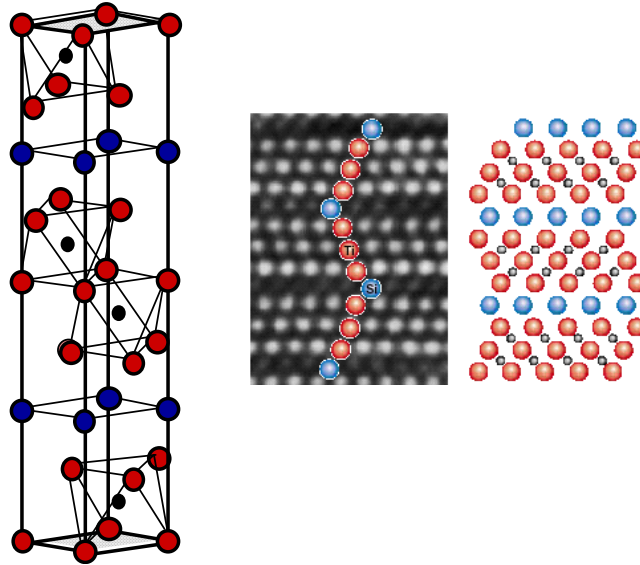


Figure 1. Typical precursor for CDC. Crystal structure of Ti_3SiC_3 (left). HRTEM lattice image of a (110) plane, showing the zigzag chains of Ti (red) and Si (blue) (center). Schematic atomic arrangement in (110) plane (right).

eliminated between 200 and 300°C. For 300°C and higher processing temperatures, the x-ray profiles showed only a broad peak at $\sim 20^\circ 2\theta$ (Cu $K\alpha$) typical of “amorphous” carbon. HRTEM after 700°C treatment showed features on the 1 nm scale but no long range order; similar images after 1200°C showed isolated regions of 2-5 small, correlated graphene fragments, too small and too sparse to show up in x-ray profiles.

Porosity was characterized by nitrogen BET, methyl chloride adsorption and small-angle x-ray scattering (SAXS). Results from the latter technique are shown in Figure 2. For monodisperse pores, the Q dependence of scattered intensity follows the Guinier relation:

$$\ln(I) \sim \exp(-Q^2 R_g^2/3)$$

where R_g = radius of gyration of the pores and $Q = 4\pi\sin\theta/\lambda$. Data from CDC's show almost monodisperse behavior; the plots in Figure 2 are nearly straight lines. More significantly, the SANS intensity increases with increasing chlorination temperature due to the increasing contrast between empty pores and carbon matrix, *i.e.* increasing pore volume. Results of a modified Guinier analysis [2] are shown in the inset, where we note that the dominant pore radius, which accounts for >95% of the pores at all processing temperatures, can be tuned with high finesse by varying the chlorination temperature. Indeed the “tuning constant” $d(\text{pore size})/dT$ is about 0.0005 nm/°C. In

practical terms, assuming +/- 10°C temperature control, pore size can be controlled to within 0.05 Å.

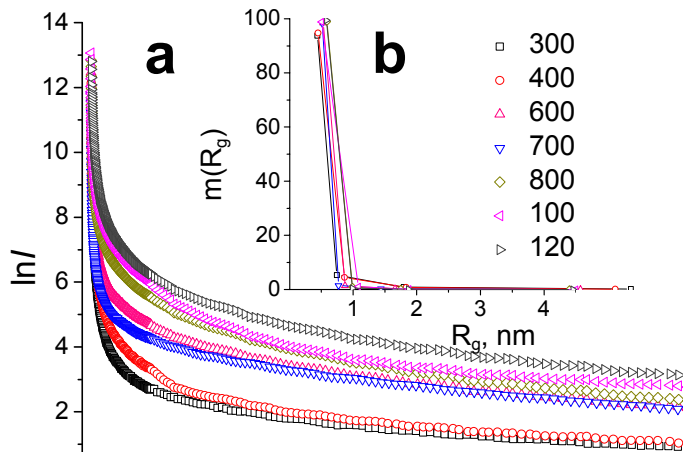


Figure 2. SAXS intensity profiles for CDC's derived from Ti_3SiC_2 by heating

Carbide	Crystal Structure	Density of the carbide, g/cm ³	Theoretical apparent density of CDC, g/cm ³	CDC porosity, %
VC	Cubic	5.48	1.04	53.6
TiC	Cubic	4.92	0.98	56.3
MoC	Hexagonal	8.8	0.98	56.5
WC	Hexagonal	15.8	0.97	57.0
β -SiC	Cubic	3.21	0.96	57.2
TaC	Cubic	14.5	0.90	59.9
ZrC	Cubic	6.56	0.76	66.0
Al ₄ C ₃	Rhombohedral	2.99	0.75	66.8
SrC ₂	Cubic	3.04	0.65	71.0
V ₂ C	Hexagonal	5.75	0.61	73.1
Ti₃SiC₂	Hexagonal	4.5	0.55	75.5
W ₂ C	Hexagonal	17.3	0.55	75.7
B₄C	Rhombohedral	2.52	0.54	76.0
Mo ₂ C	Hexagonal	9.12	0.54	76.2
BaC ₂	Cubic	3.57	0.53	76.3
Fe ₃ C	Orthorhombic	7.4	0.49	78.1
Ta ₂ C	Hexagonal	15	0.48	78.6
Nb ₂ C	Hexagonal	7.85	0.48	78.9
Cr ₄ C	Cubic	6.99	0.38	83.1

The table above summarizes the ideal properties of CDC's obtained by complete chlorination of a variety of precursors. Compounds in bold face are under active study.

Conclusions

The large pore volume and tunability of pore size in CDC's suggest that they might satisfy the 6 wt.% hydrogen storage criterion for the Clean Car Project. We are beginning a program to measure hydrogen capacities, heats of adsorption and desorption, kinetics and cyclability using a variety of neutron scattering methods, all of which are very sensitive to, and specific for, hydrogen in carbon. Excellent accuracy for the H/C ratio can be achieved with 0.1 – 1.0 gram samples, and *in situ* experiments (e.g. H concentration during loading or unloading) are straightforward.

References

- [1] Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J. E. Fischer, B. Ye, H. Foley and M. Barsoum, *Nature Materials* **2**, 591(2003).
- [2] R. N. Kyutt *et al.*, *Phys. Solid State* **41**, 1359 (1999).