Supporting information for:

Molecular Modeling of Microporous Structures of Carbide-Derived Carbon Based Supercapacitors

Sabine Schweizer,[†] Robert Meissner,[‡] Marc Amkreutz,[‡] Karsten Thiel,[‡] Peter Schiffels,[‡] Johannes Landwehr,[¶] Bastian J. M. Etzold,[¶] and Jörg-Rüdiger Hill[*,†]

[†]*Scienomics GmbH, Bürgermeister-Wegele-Straße 12, 86167 Augsburg, Germany*

[‡]*Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung IFAM - Klebtechnik und Oberflächen -, Wiener Straße 12, 28359 Bremen, Germany*

[¶]*Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Technische Universität Darmstadt, Alarich-Weiss-Straße 8, 64287 Darmstadt, Germany*

E-mail: joerg-ruediger.hill@scienomics.com

Phone: + 49 (0) 821 450 165 60. Fax: + 49 (0) 821 450 165 62

Simulation set-ups

In the following, a short description of the different simulation set-ups (A) - (E) is provided.

Set-up (A)

1. 50 ps NVT @ RT
2. 200 ps NPT @ 2500 K
3. Quenching from 2500 K to RT with quench rate of $2.2 \cdot 10^{12}$ K/s in NPT ensemble
4. Removal of all Si atoms
5. 200 ps NVT @ RT

Set-up (B)

1. 50 ps NVT @ RT
2. 200 ps NPT @ 2500 K
3. Quenching from 2500 K to RT with quench rate of $1.1 \cdot 10^{13}$ K/s in NPT ensemble
4. Removal of all Si atoms
5. 200 ps NVT @ RT

Set-up (C)

1. 50 ps NVT @ RT
2. 200 ps NPT @ 500 K
3. Quenching from 500 K to RT with quench rate of $2.2 \cdot 10^{12}$ K/s in NPT ensemble
4. Removal of all Si atoms

5. 200 ps NVT @ RT

Set-up (D)

1. Removal of all Si atoms
2. 50 ps NVT @ RT
3. 200 ps NVT @ 2500 K
4. Quenching from 2500 K to RT with quench rate of $2.2 \cdot 10^{12}$ K/s in NVT ensemble
5. 200 ps NVT @ RT

Set-up (E)

1. Removal of all Si atoms
2. 50 ps NVT @ RT
3. 200 ps NVT @ 500 K
4. Quenching from 500 K to RT with quench rate of $2.2 \cdot 10^{12}$ K/s in NVT ensemble
5. 200 ps NVT @ RT

Maximum pore size

In this section, the diameter of the largest included sphere (also denoted as maximum pore size) is listed for the various simulation set-ups. The analysis was carried out using the software tool Zeo++.[S1,S2]

Table S1: Diameter of the largest included sphere (D_i) in Å obtained for the final structure following the different simulations set-ups (A)-(E) (details see above).

setup	D_i
(A)	9.7
(B)	9.6
(C)	9.2
(D)	12.7
(E)	9.8

Table S2: Diameter of the largest included sphere (D_i) in Å obtained for the final structure of the different SiC polytypes following set-up (A).

setup	D_i
4H-SiC	9.8
6H-SiC	9.6
3C-SiC	9.0

Table S3: Diameter of the largest included sphere (D_i) in Å obtained for the final structure of the 2x2x2 SiC supercell.

setup	D_i
5 ns NVT	11.4
10 ns NPT	9.7

Table S4: Diameter of the largest included sphere (D_i) in Å obtained for the final structure 4H-SiC-based carbon structure after longer equilibration in the NVT and NPT ensemble.

setup	D_i
1 ns NVT	9.6
1 ns NPT	9.1
10 ns NVT	9.3
30 ns NPT	8.9

Density and cell parameters

In this section, the density and the cell parameters a, b, c of the final microporous carbon structures are listed for the different simulation set-ups. The results were obtained using MAPS software.[S3]

Table S5: Density in g/cm^3 and cell parameters in Å obtained for the final structure following the different simulations set-ups (A)-(E)

	(A)	(B)	(C)	(D)	(E)
Density	0.98	0.98	0.98	0.97	0.97
a	61	61	61	62	62
b	61	61	61	62	62
c	60	60	60	60	60

Table S6: Density in g/cm^3 and cell parameters in Å of the 4H-SiC-based carbon structure after equilibration in the NPT ensemble.

	1 ns NPT	30 ns NPT
Density	1.11	1.10
a	59	59
b	59	59
c	58	58

Table S7: Density in g/cm^3 and cell parameters in Å of 2x2x2 supercell.

	5 ns NVT	10 ns NPT
Density	0.98	1.10
a	123	118
b	123	118
c	120	116

Table S8: Density in g/cm^3 and cell parameters in Å obtained for the final structure of the different SiC polytypes following set-up (A)

	4H-SiC	6H-SiC	3C-SiC
Density	0.98	0.98	0.98
a	61	61	61
b	61	61	61
c	60	60	61

Ring size

In the following, details of the ring size analysis performed with polypy[S4] are provided. The number of five- to seven-membered rings are given as well as the total number of rings identified using polypy.

Table S9: Total number and number of five- to seven-membered rings for the different simulation set-ups (A)-(E).

Ring size	(A)	(B)	(C)	(D)	(E)
5	0	15	14	126	19
6	87	642	768	1257	779
7	49	374	367	817	439
sum	1056	1031	1149	2200	1237

Table S10: Total number and number of five- to seven-membered rings of 4H-SiC-based carbon after longer equilibration in the NVT and NPT ensemble.

	1 ns NVT	30 ns NPT
5	20	24
6	720	736
7	371	487
sum	1111	1247

Table S11: Total number and number of five- to seven-membered rings of the 2x2x2 supercell.

	5 ns NVT	10 ns NPT
5	189	203
6	5891	6454
7	3332	3761
sum	9412	10418

Table S12: Total number and number of four- to seven-membered rings of the different SiC polytypes.

	4H-SiC	6H-SiC	3C-SiC
4	0	0	1
5	20	27	28
6	687	686	860
7	349	363	447
sum	1056	1076	1336

Coordination number

In this section, the coordination number of the carbon atoms in the final structures are provided. Numbers in parentheses refer to carbon atoms with two bond partners and enclosing an angle of 120°, i. e. atoms that can be sp^2-hybridized, and carbon atoms having three bond partners and showing a deviation of 10° or more from planarity, i. e. atoms that can be sp^3-hybridized.

Table S13: Coordination number of the carbon atoms in the final structures as obtained following the different simulation set-ups (A)-(E).

	(A)	(B)	(C)	(D)	(E)
0	16	12	7	0	0
1	141	155	126	14	100
2	4189	4250	4164	2059	3879
3	5197 (4189)	5125 (4250)	5254 (4164)	7392 (2051)	5560 (3878)
4	57 (1459)	58 (1379)	49 (1449)	135 (4313)	61 (1930)

Table S14: Hybridization in percent of the carbon atoms in the final structures as obtained following the different simulation set-ups (A)-(E).

	(A)	(B)	(C)	(D)	(E)
sp	0.0	0.0	0.0	0.1	0.0
sp^2	83.9	84.8	84.2	53.5	79.0
sp^3	16.1	15.2	15.8	46.4	21.0

Table S15: Coordination number of the carbon atoms in the final structures after longer equilibration in the NVT and NPT ensemble.

	1 ns NVT	30 ns NPT
0	16	6
1	126	74
2	4054	3668
3	5346 (4054)	5786 (3668)
4	58 (1599)	66 (2266)

Table S16: Hybridization in percent of the carbon atoms in the final structures after longer equilibration in the NVT and NPT ensemble.

	1 ns NVT	30 ns NPT
sp	0.0	0.0
sp^2	82.5	75.5
sp^3	17.5	24.5

Table S17: Coordination number of the carbon atoms in the final structures of the 2x2x2 supercell.

5 ns NVT	10 ns NPT
60	45
907	642
31700	29316
43651 (31700)	46274 (29316)
482 (14528)	524 (18233)

Table S18: Hybridization in percent of the carbon atoms in the final structures of the 2x2x2 supercell.

	1 ns NVT	30 ns NPT
sp	0.0	0.0
sp^2	80.2	75.4
sp^3	19.8	24.6

Table S19: Coordination number of the carbon atoms for the different SiC polytypes.

	4H-SiC	6H-SiC	3C-SiC
0	16	10	16
1	141	126	146
2	4189	4268	4825
3	5197 (4189)	5132 (4267)	5920 (4825)
4	57 (1459)	65 (1439)	69 (1626)

Table S20: Hybridization in percent of the carbon atoms for the different SiC polytypes.

	4H-SiC	6H-SiC	3C-SiC
sp	0.0	0.0	0.0
sp^2	83.9	84.1	84.3
sp^3	16.1	15.9	15.7

Monte Carlo simulations

Probabilities NPT simulations

- Center-of-mass molecule translation move: 0.49
- Rotation about the center-of-mass move: 0.50
- Isotropic volume move: 0.01

Probabilities Gibbs-NPT simulations

- Center-of-mass molecule translation move: 0.25
- Rotation about the center-of-mass move: 0.25
- Configuration-bias two molecule transfer move: 0.25
- Rotational two molecule transfer move: 0.24
- Isotropic volume move: 0.01
- All probabilities to perform moves on carbon were set to 0.0.

Calculation of the specific volume

The specific volum V_{spec} is calculated as follows:

$$V_{spec} = \frac{V_{ads}}{m_C} \tag{1}$$

with

$$V_{ads} = \frac{N_{CO_2} k_B T}{p} \tag{2}$$

and

$$m_C = \frac{N_C}{N_A M_C} \tag{3}$$

where

N = Number of molecules

k_B = Boltzmann constant / J K^{-1}

T = Temperature / K

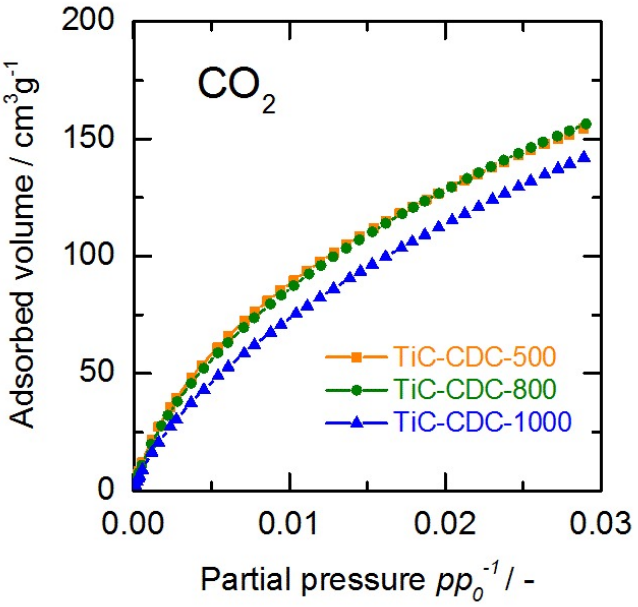
p = pressure / Pa

m = mass / kg

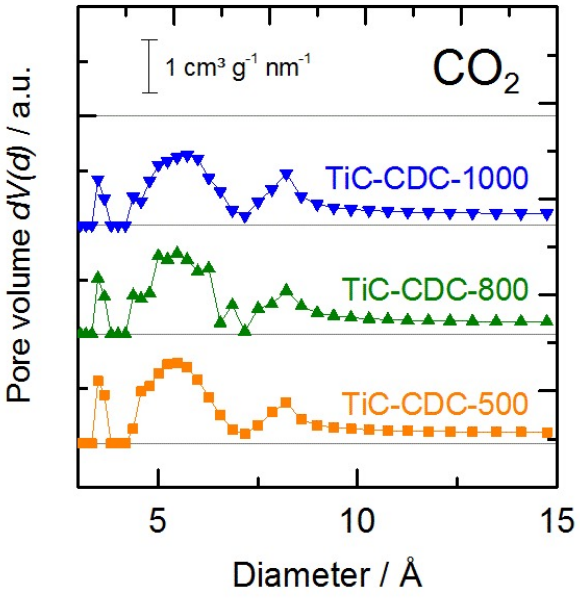
N_A = Avogadro number / mol^{-1}

M = molar mass

CO_2 adsorption analysis



(a)



(b)

Figure S1: Physisorption measurements based on CO_2 adsorption at 0 °C using the instrument NOVA 4200e from Quantachrome Instruments. Preatreatment of all samples was at 100 °C for 24h. The isotherms are shown in (a) and the differential pore volumes in (b).

References

(S1) Willems, T. F.; Rycroft, C. H.; Kazi, M.; Meza, J. C.; Haranczyk, M. *Microporous and Mesoporous Materials* **2012**, *149*, 134 – 141.

(S2) Martin, R. L.; Smit, B.; Haranczyk, M. *J. Chem. Inf. Model.* **2012**, *52*, 308–318.

(S3) Scienomics, MAPS version 3.4.1. 2014; `www.scienomics.com`.

(S4) Polypy. http://sourceforge.net/projects/polypy/, 2014.