

BIOMORPHIC DERIVED MICROPOROUS CARBONS AS NATURAL GAS STORAGE MATERIALS

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Introduction

Using natural gas as an automotive fuel exhibits several considerable advantages like lower vehicle emissions and lower fuel costs compared to gasoline. Nevertheless the low volumetric energy density and consequently the resulting low driving range make it unattractive for the application in vehicles [1]. Much effort is carried out to increase the volumetric energy density. One promising possibility to improve the volumetric energy density is the storage of natural gas by adsorption in microporous materials. By the usage of adsorbents the required pressure could be decreased to 3.5 MPa. In contrast, pressures in the range of 20 MPa are necessary to store natural gas by compression. Activated carbons (AC) and carbide-derived carbons (CDCs) are materials with high micropore surface area and micropore volume. Considering the isothermal gas storage these materials improve the storage capacity in comparison to compressed natural gas storage systems and reach in isothermal ideal measurements the required value of 180 V/V. However this value could not be reached in experiments under realistic, technical conditions yet [2]. The occurring heat of adsorption during realistic experiments leads to hot spots within the powder beds during fast charging processes and the total gas storage capacity, which is strongly dependent on the temperature, is decreased. A novel approach to overcome this problem is the usage of structured storage material systems. These systems offer higher heat conductivities resulting in minimized temperature rises during the gas charging process. Consequently the achievable storage capacity can be improved. To create those structured adsorbents a three step synthesis route is carried out:

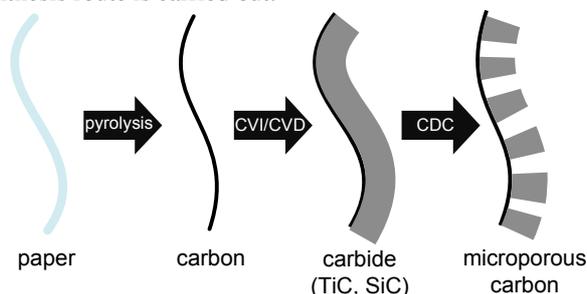


Figure 1: Three step synthesis route for the preparation of microporous gas storage materials

Within a first step paper preforms are converted into biocarbon by a pyrolysis reaction. In the course of this reaction macroporous fibers consisting of cellulose are

converted into carbon, while the fiber structure needs to be retained. Afterwards the formed carbon fibers are coated with carbides (TiC, SiC) by a chemical vapor deposition (CVD) process. Finally microporous carbon structures are achieved by treating the structures by the CDC-method [3,4]. Here the non-carbon compound of the deposited carbide is etched selectively by a high temperature (800°C – 1200°C) chlorine gas treatment and removed by the gas flow. During the etching microporous carbon remains and the original carbide structure stays unchanged. By varying the reaction temperature or carbide precursor a tailoring of the resulting pore size distribution is possible [3].

Experimental

Within the first step paper preforms (e.g. filter papers, felts, felt papers) were pyrolysed at 1123 K under Helium atmosphere for one hour. By a CVD-step titanium and silicon carbide were deposited on the pyrolysed paper preforms. During the TiC deposition titanium tetrachloride and methane were used as precursors whereas methyltrichlorosilane was used for the SiC deposition. Both deposition reactions were carried out for 4 h. The TiC deposition took place at 1373 K, the SiC deposition reaction at 1223 K. The etching reaction was carried out at 1073 K. The gaseous chlorine treatment was performed for 4 – 8 hours. All reactions of the synthesis route were performed in a horizontal hot wall tubular reactor. The gas storage behavior of the produced materials was characterized experimentally by measuring the amount of stored and discharged methane and the development of the temperature at different charging rates.

Results and Discussion

To prove the unchanged fiber structures after each step scanning electron microscope pictures were taken. Within the pyrolysis step weight losses up to 80% after the treatment of all initial paper preforms were determined. To achieve high storage capacities concerning the methane storage the amount of pyrolysed papers compared to the amount of the gas storing carbide-derived carbon should be as low as possible. Thus low paper densities and high CVD deposition amounts are favored. During the second step, the CVD-process, titanium and silicon carbide were deposited on the pyrolysed papers. The stability of the achieved structures is strongly dependent on the density of the initial materials. For raw materials with densities above 750 kg m⁻³ spalling of the coating occurred. The aim of the deposition step is to achieve high mass gains because the microporous carbon which increases the gas storage is created directly out of the carbide by the chlorine treatment afterwards. Mass gains up to 3165 wt.-% and 2682 wt.-% could be achieved for crepe papers coated with TiC respectively with SiC.

Finally microporous carbon was introduced to the carbide coated on biomorphic structures by a high temperature chlorination reaction. Figure 2 shows the dependency between the resulting SSA and the conversion for biomorphic SiC-DC materials:

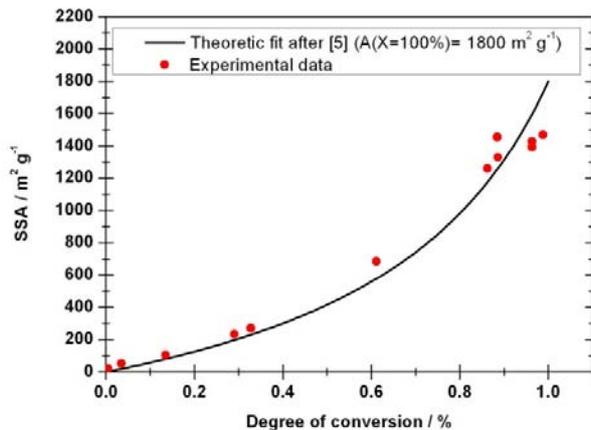


Figure 2: Specific surface area versus conversion; 3 different papers used (felt, felt-paper, filter paper): CVI-SiC: $t = 4$ h, $T = 950$ °C, $v = 0.24$ m s⁻¹, $x_{\text{CH}_3\text{SiCl}_3} = 0.08$, $V_{\text{H}_2} : V_{\text{CH}_3\text{SiCl}_3} = 2$; CDC: $T = 800$ °C, $v = 0.015$ m s⁻¹, 9.35-18.69 vol.-% Cl₂, $t = 3$ -8 h; SSA from CO₂- Sorption measurement and DFT evaluation, DFT Error < 0.11 %

Figure 2 shows a non-linear correlation between the micropore surface area (evaluated from CO₂-sorption measurements) and the conversion like proposed by Becker et al. [5]. In Figure 2 the pore size distribution for pores smaller than 1.5 nm are given for titanium- and silicon carbide-derived carbon felt materials (determined by CO₂-sorption and DFT evaluation). The cumulative pore areas for TiC-DC and SiC-DC felt materials illustrated in Figure 2 area are nearly the same. Despite less conversion the TiC-DC felt achieved the same specific surface area in comparison to the SiC-DC felt. Consequently totally converted TiC-DC biomorphic materials can offer a higher amount of SSA for gas storage compared to SiC.

The methane uptakes of the synthesized biomorphic carbide-derived carbon materials were tested in a pressure range between 10 mbara and 5 MPa at ambient temperature. The highest uptake could be achieved by using SiC-DC material derived from handcrafted felt with a SSA of 1411 m² g⁻¹. For a flow rate of 15 ml_N min⁻¹, which corresponds to a charging time of 50 min, 14.9 wt-% methane could be stored within the material at 3.5 MPa and 298 K (degassing for 2 hours at 400 K). By increasing the charging volume flow the storage capacity of the material decreased because temperature rises within the material occur. Consequently the storage capacity at a volume flow of methane of 1000 ml_N min⁻¹ (45 sec. charging) was reduced to 8.0 wt-%, due to a temperature rise of 38.4 K within the materials. Other after the same route produced adsorbents were tested and showed similar charging behavior.

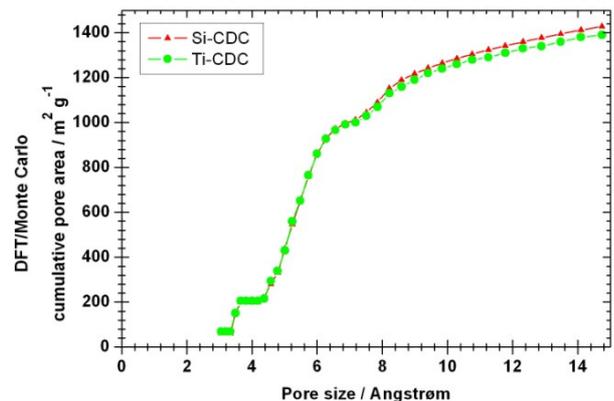


Figure 3: CO₂-sorption of TiC-DC felt (etching 89%) and SiC-DC felt (etching 96%); Model: Adsorbate Carbon NL-DFT Slit-Pores, Fitting Error < 0.11 %

Conclusion

Microporous gas storage materials out of biomorphic basic materials could be synthesized by a three step route which consists of a pyrolysis reaction, a carbide deposition reaction and the carbide-derived carbon. The produced materials were tested concerning their methane uptake at realistic charging conditions and showed promising gas storage behavior. Methane uptakes up to 14.9 wt-% could be realized. TiC-DC derived out of biomorphic materials achieved higher uptakes in comparison to SiC-DC structures. Further optimizations are going to be carried out concerning the absorbent itself and the bulk structure to improve the heat management within the structures realizing faster charging processes.

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