



# Porous and high surface area silicon oxycarbide-based materials—A review



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## ABSTRACT

Silicon oxycarbide (SiOC)-based materials are a class of polymer-derived ceramics that enables the formation of a homogeneous structure at the molecular level starting from polymer precursors. In this system, oxygen and carbon atoms share bonds with silicon atoms in the amorphous network structure while elemental carbon, and possibly nanosized SiO<sub>2</sub> and SiC nanodomains may co-exist. Because of the flexibility of molecular level composition and microstructure designs, the systems can be made porous with high specific surface areas by changing the precursor compositions and the ceramization conditions. In this review, two strategies of creating porous SiOCs are discussed: conventional approach of using fugitive fillers, as well as pore formation and selective removal of certain SiOC matrix compositions (such as carbon, SiO<sub>2</sub>, or SiC) at the molecular level. For the former, it includes ceramic replication of an organic template, direct foaming, and sacrificial pore formers. For the latter, it includes molecular level pore formation, molecular level species removal, and SiOC porous network creation through molecular templates. Direct pore formation can be achieved by changing processing conditions, using different precursor architectures, and using different hydrosilylation agents. For SiOC porous network creation through molecular level species removal, it includes molecular level free carbon removal, molecular level SiO<sub>2</sub> nanocluster removal, and molecular level carbon removal from SiC (and possibly BC<sub>x</sub> for SiOBC). To understand single nanometer (<10 nm) pore formation and phase separation for selective species removal, SiOC nanostructure models and composition descriptions after the pyrolysis are explained.

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**Abbreviations:** D<sub>4</sub><sup>H</sup>, 2,4,6,8-tetramethylcyclotetrasiloxane; DVB, divinylbenzene; <sup>H</sup>MM<sup>H</sup>, 1,1,3,3-tetramethyldisiloxane; NLDFT, non-linear density functional theory; PDMS, poly(dimethylsiloxane); PHMS, poly(hydridomethylsiloxane); PMMA, poly(methyl methacrylate); PSO, polysiloxane; Q(M<sup>H</sup>)<sub>4</sub>, tetrakis(dimethylsiloxy)silane; SiOC, silicon oxycarbide.

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## 1. Overview of high surface area SiOC materials

Porous and high surface area materials have important applications as sensors, chemical reactors, electrodes, gas storage media, molecular sieves, membrane supports, lightweight structural materials, thermal insulators, bioimplants, among others. On this front, much work has been done for room temperature use materials, such as porous carbons, mesoporous silicates, metal-organic frameworks, and organic frameworks. However, many applications require the porous materials to be thermally stable and the specific surface area to be higher than a couple of hundred square meters per gram. Thermally stable and high surface area materials are seriously lacking. This can be attributed to two factors: the instability of the matrix itself (sintering, decomposition) and the instability of the pores (shrinkage, closure) with temperature increase. These challenges call for the development of new, highly porous materials with stable networks. Building up porous materials from polymer precursor molecular units and tailoring the polymer molecular structure to ceramic transformation so that high surface area and thermally stable phases can be consistently produced are of great scientific and technological significance [1,2]. SiOC porous materials are such a unique system that can be produced from a large variety of polysiloxane (PSO) precursors and a wide range of processing conditions. A wide array of interesting SiOC microstructures can be created to offer highly porous materials with the thermal stability from a few hundred degrees Celsius to 1300 °C.

From the composition point of view, SiOC is an exciting high temperature material system that enables the formation of a homogeneous amorphous-nanocrystalline mixed structure at the molecular level starting from polymer precursors containing Si-H, Si-Me, Si-Et, Si-Vy, or Si-Ph bonds. SiOC ceramics, prepared from preceramic polymer routes, can be thermochemically stable up to 1200 °C in air, and do not show compositional or microstructural changes after fairly extended periods of time at elevated temperatures. They have good oxidation resistance, possess a low coefficient of thermal expansion, and exhibit good mechanical strength, creep resistance, and resistance to corrosion [3]. However, after extended time at 1200 °C or higher, the stability of SiOC deteriorates due to the evolution of porosity, the oxidation of different species, and the devitrification of the SiOC matrix [4–6]. The compositions and the structural characteristics of these materials change continuously with the precursors and the temperatures used to process the precursors and any filler that might be employed. The chemical compositions may be controlled by varying the molecular architecture of organosiloxane precursors as well as the temperature and atmosphere of pyrolysis [7]. Depending on the pore forming process, the pore sizes for SiOC can vary greatly from nanometers to millimeters and lead to large ranges of porosity and specific surface area [2].

Polymer-derived SiOC materials have the advantages of amendable to polymer-processing techniques, homogeneity of precursors at the molecular level, relatively lower processing temperatures (compared to conventional ceramic processing methods), and possible synthesis of new compositions that can have functional properties, such as electrical conductivity and magnetic property (Fig. 1). More importantly, polymer-derived SiOCs can be formed from different polymer molecular structures so that the resulting nano- and/or micro-structures and phases can be tailored [1].

In general, there are two ranges of pores that can be created for a SiOC material. One kind of pores is in the submicron to tens-thousands of microns range. This type of SiOC is generally produced using fugitive fillers or other types of pore forming processes with the following approaches: ceramic replication of an organic template, direct foaming, and sacrificial pore formers. The SiOC matrix may be dense or porous and serves the major function of a connecting skeleton for the porous materials. The starting polymer precursors can vary greatly but the small, single-nanometer pores (if there is any) in the SiOC matrix do not make significant contribution to the overall porosity. This pore forming strategy can be labeled as conventional SiOC porous material formation process. The advantage of such porous materials is the easy accessibility of the pores by liquid, gas, and even other agents for different applications due to their large sizes. The shortcoming is the low mechanical properties. The other kind of porous SiOC materials has pores in the single nanometer to at most tens of nanometers range. These pores are created at two stages: volatile species formation during the pyrolysis (direct pore formation, different precursor architectures) or selective species removal after the pyrolysis based on the phase separated domains (free carbon removal, SiO<sub>2</sub> nanocluster removal, and carbon removal from SiC). The advantages of such porous structures are their ultrahigh specific surface areas, small pore sizes, and narrow pore size distributions. However, the accessibility of such small pores can be an issue for certain applications.

In this review, the above two strategies of creating porous SiOCs will be discussed. To understand single nanometer pore formation and phase separation for the selective species removal approach, the SiOC nanostructure models and composition interrelationships after the pyrolysis are explained.

## 2. Conventional SiOC porous material formation

### 2.1. Ceramic replication of an organic template

To form SiOC porous materials with pores in the single micron to hundreds or even thousands of microns range, using organic template is the most intuitively straightforward process. First, organic templates can be environmentally benign and cost effective. Second, organic templates can be easily removed to create pores. In certain cases, organic materials may also contain

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