



## Silicon oxycarbide-derived carbons from a polyphenylsilsequioxane precursor for supercapacitor applications



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### ABSTRACT

In this study, we report on the preparation of new silicon oxycarbide-derived carbons (SiOCD) obtained by pyrolysis and chlorination of a polyphenylsilsequioxane pre-ceramic precursor. Wet-chemical conversion of phenyltrimethoxysilane (PhTMS) to the organosilica material was conducted using a two-step acid/base sol–gel process in aqueous medium. The resulting material was subsequently pyrolysed at 700, 1000 and 1300 °C to obtain a non-porous silicon oxycarbide ceramic. Chlorination at 700 and 1000 °C led to carbons having large surface areas exceeding 2000 m<sup>2</sup> g<sup>-1</sup> as well as large micro-/mesopore volumes up to 1.4 cm<sup>3</sup> g<sup>-1</sup>. The temperature of the thermal treatment significantly influences the carbon and final pore structure. Pyrolysis at 700 °C and subsequent chlorination at 700 °C led to a mainly microporous material, whereas pyrolysis at 1300 °C and subsequent chlorination at 1000 °C generated a hierarchically porous SiOCD with micro- and mesopores, respectively. All SiOCD materials were prepared as supercapacitor electrodes using an aqueous slurry containing polytetrafluoroethylene (PTFE) and sodium carboxymethyl cellulose (CMC) as binder. With an organic electrolyte (1 M TEABF<sub>4</sub> in acetonitrile) capacitances of up to 110 F g<sup>-1</sup> and good long term stabilities could be observed.

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### 1. Introduction

Electrochemical energy storage devices become progressively more important for mobile and stationary applications. Up to now, batteries and supercapacitors complement each other. On the one hand, batteries show large energy densities (for example 120–200 Wh kg<sup>-1</sup> for modern lithium ion batteries [1]) but still suffer from slow charge/discharge characteristics and poor cycle life. In contrast, porous carbon based supercapacitors show at best 10% of the energy density of lithium ion batteries. Supercapacitors may roughly be distinguished into three groups [2,3]: True electrical double layer capacitors (EDLCs), pseudocapacitors, and lithium

ion hybrid capacitors. In EDLCs, the electrodes consist of porous carbons. Immersed into an electrolyte, ions will be adsorbed on the carbon surface to form an electrical double layer if a potential is applied. They may be charged and discharged in seconds for more than 1 million cycles.

Many efforts have been made in recent years to develop novel carbon materials for energy storage applications [2–8]. Among them, carbide-derived carbons (CDCs) are interesting candidates. Because CDCs are a special class of highly microporous carbons with surface areas exceeding 2000 m<sup>2</sup> g<sup>-1</sup> and thus they are suited well for several potential applications such as gas [9–11] and energy storage [6,12,13] as well as catalysis [14]. CDCs are obtained by high temperature chlorination of carbides. The metals or metalloids are extracted as gaseous chlorides leaving behind the highly porous carbon. Due to the layer-by-layer metal extraction a precise control of the porosity of the final carbon material is possible. Gogotsi and co-workers were the first to demonstrate the possibility to tune the micropore size for a Ti<sub>3</sub>SiC<sub>2</sub> material [15]. By variation of the chlorination temperature between 200 and 1200 °C the pore size could be tailored from 0.3 to 0.8 nm, with almost a linear dependence between pore size and chlorination temperature. The

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possibility to tune the micropore size also allowed for a detailed investigation of the influence of pore size on double layer capacitance. By reducing the pore size to values below 1 nm an enormous increase in capacitance was obtained. Specific capacitance may exceed the barrier for activated charcoal of  $100 \text{ F g}^{-1}$  to values well above  $150 \text{ F g}^{-1}$  (with an organic electrolyte). The enormous increase in capacitance is best explained by a distortion of the electrolyte shell within small micropores (<1 nm) and thus a stronger adsorption of the ion centre to the pore surface [16].

According to the facile chlorination process it is possible to transform carbides in various shapes and nanostructures by maintaining the structural features. For instance, Chmiola et al. recently converted monolithic TiC plates with  $300 \mu\text{m}$  thickness into the corresponding monolithic CDC. From this material a micro-supercapacitor device was fabricated which showed volumetric capacitances exceeding those of conventional CDCs by a factor of 2 [17]. Yushin and co-workers have recently demonstrated the conversion of a periodically mesostructured silicon carbide to give a hierarchically porous CDC where the initial pore walls of the SiC now contain a large micropore volume [18]. This material is promising as electrode material for supercapacitors since the mesopores allow fast ion transport throughout the particles. Thus these carbons demonstrate outstanding capacitance values at large currents. However, the synthesis of this material involves a nanocasting step with a rather expensive polycarbosilane. Therefore much cheaper routes have to be found for industrial applicability.

Sol-gel processing is a facile, cheap and environmentally-friendly tool for the preparation of various pre-ceramic materials in various shapes such as powders, films or monoliths [19]. Especially in the case of organosilanes, reaction kinetics are quite slow and allow precise control of hydrolysis and condensation reactions and so the final molecular structure, porosity and morphology. Pyrolysis of organosilica materials at temperatures up to  $1000^\circ\text{C}$  leads to a rearrangement of silicon, carbon and oxygen bonds to form a complex network, where silicon is bound to oxygen and carbidic carbon and a free carbon phase is formed as a by-product. The final composition of the silicon oxycarbide strongly depends on factors such as the organosilane precursor itself, e.g. type and length of side chains, or the microstructure of the polymer [20–22]. Very recently, silicon oxycarbides were shown to be valuable CDC precursors. Gogotsi et al. pyrolysed and chlorinated pre-condensed polyorganosilsesquioxanes [23]. The resulting silicon oxycarbide-derived carbon (SiOCDC) is characterised by a hierarchical pore structure due to the presence of mesopores, which are probably obtained due to larger silica or carbon domains formed during pyrolysis. In the same work, excellent gas adsorption properties for hydrogen and methane were demonstrated. However, there was no report on the electrochemical properties.

In this manuscript, the chlorination of sol-gel derived silicon oxycarbide materials and the influence of the preparation parameters on the performance of SiOCDC as supercapacitor electrodes are investigated in detail. In Fig. 1, the synthesis procedure is schematically demonstrated. Phenyltrimethoxysilane (PhTMS) is used as sol-gel precursor for the formation of SiOC materials via pyrolysis in inert atmosphere. PhTMS is one of the cheapest silanes available

and is hence suitable with respect to cost reduction for a scale-up. Different pyrolysis and chlorination parameters were investigated with regard to structural build up and pore formation as well as their influence on the electrochemical properties. It is also demonstrated that quite good long term stability can be reached for the resulting carbons when they are processed as EDLC electrode materials using an aqueous slurry containing PTFE and sodium carboxymethyl cellulose (CMC) as a novel binder. The mixture of both binding agents shows the best mechanical stability in comparison with the pure binders. Thus, a reduction of the amount of halogenated polymer in the electrode by partial substitution of polytetrafluoroethylene with carboxymethyl cellulose is possible.

## 2. Experimental

### 2.1. Materials

The silicon oxycarbide derived carbons (SiOCDCs) were synthesised via pyrolysis and chlorination of a xerogel precursor (Fig. 1). The precursor was formed using a sol-gel process reported by Liu et al. [24]. The gels were produced in a two-step process at room temperature. In a typical synthesis approach, 99.15 g (0.5 mol) Phenyltrimethoxysilane (PhTMS; 94%+, Sigma Aldrich) were mixed with 72.06 g (4 mol) of water and then the pH value was adjusted to 2 by adding 1 M HCl (Sigma Aldrich). After 2 h of hydrolysis, a 2 M solution of NaOH (Grüssing GmbH) was added until the pH value reached 7. The gels formed were heated for 3 d at  $80^\circ\text{C}$  in order to evaporate the solvent. The xerogels were pyrolysed under Ar atmosphere at the respective temperatures ( $700$ ,  $1000$  and  $1300^\circ\text{C}$ ) forming silicon oxycarbides (SiOCs). In the heat treatment a ramp of  $150^\circ\text{C h}^{-1}$  is used. The final temperature during pyrolysis was held for 3 h in the tube furnace and then cooled to room temperature under Ar atmosphere. Subsequently, the oxycarbides were etched at temperatures of  $700$  or  $1000^\circ\text{C}$  in a stream of  $80 \text{ ml min}^{-1} \text{ Cl}_2$  and  $70 \text{ ml min}^{-1}$  argon followed by a treatment with  $\text{H}_2$  at  $600^\circ\text{C}$  for 1 h to remove remaining chlorine in the samples forming SiOCDCs.

### 2.2. Electrode preparation

In a typical electrode preparation, 90 mg of the active material and 5 mg of each binding agent were used. The as-made material was mixed with sodium carboxymethylcellulose (NaCMC; technical grade, VWR) and polytetrafluoroethylene (PTFE; 60 wt.% dispersion in water, Sigma Aldrich) in an aqueous solution resulting in a 5 wt.% concentration for each binding agent in the final electrodes. The mixture was homogenised for 1 h in a ball mill with a power of 30 W. The resulting slurry was cast on a carbon-coated aluminium foil from Exopack Advanced Coatings (UK) with a coating speed of  $50 \text{ mm s}^{-1}$  using an electrical doctor blade (MTV Messtechnik OHG). The thickness of the wet film was adjusted to  $120 \mu\text{m}$ . Round shaped electrodes with 10 mm diameter were blanked from the dried films and activated in a vacuum oven at  $120^\circ\text{C}$  for more than 12 h.

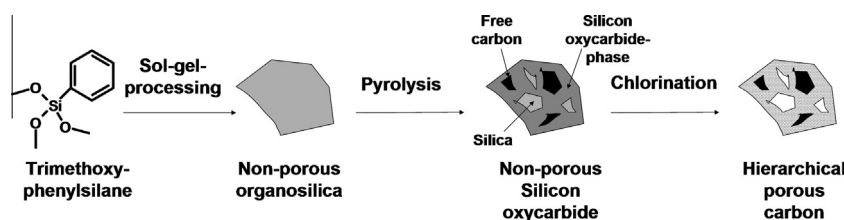


Fig. 1. Scheme of SiOCDC synthesis.

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