



# The influence of pyrolysis temperature on the electrochemical behavior of porous carbon-rich SiCN polymer-derived ceramics



Mathias Storch, Dragoljub Vrankovic\*, Magdalena Graczyk-Zajac, Ralf Riedel

Department of Materials and Earth Sciences, Technical University Darmstadt, Germany

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## ABSTRACT

Within this study we report on the impact of the pyrolysis temperature on the structural and electrochemical properties of porous carbon-rich polymer-derived silicon carbonitride (SiCN) ceramics. Microstructural features of the synthesized materials were characterized in detail and discussed with respect to the lithium storage properties. X-ray diffraction study reveals the amorphous nature of the pyrolysed ceramics up to 1100 °C, while a crystalline SiC-phase is formed at 1400 °C. Micro-Raman spectroscopy shows that pyrolysed samples contain a free disordered carbon phase which tends to order with increasing pyrolysis temperature. Galvanostatic cycling with potential limitation enables to monitor the lithiation and delithiation performance. High irreversible losses are identified during the first cycle lithiation due to formation of SEI. Nevertheless the highest electrode capacities are recorded for the sample pyrolysed at 900 °C reaching a first cycle reversible capacity of 447 mAh·g<sup>-1</sup> and a 100th cycle reversible capacity of 534 mAh·g<sup>-1</sup> at a current of 72 mA·g<sup>-1</sup>. Further it is found that the prepared materials offer improved high current lithium storage ability compared to dense SiCN ceramics reported in literature so far.

## 1. Introduction

The Lithium-ion battery is one of the most common energy storage devices used in consumer electronics, also successfully implemented into electric vehicles. Therefore high energy and power densities as well as long lifetime are required and need to be improved. One possible way to improve the lithium-ion battery can be the exchange of active materials. It has been already shown that polymer-derived ceramics (PDCs), in particular carbon-rich SiOC and SiCN represent an interesting group of potential negative electrode materials [1–4]. Promising results on the polysilazane derived ceramic materials pyrolysed at 1000 °C possessing high reversible capacities (520 to 540 mAh·g<sup>-1</sup>) were reported by Dahn et al. in 1997 [1]. Additionally, blending the preceramic polymer with different amounts of pitch resulted in 450 mAh·g<sup>-1</sup> for a high content of pitch (75%) and 560 mAh·g<sup>-1</sup> for a low pitch content (25%). In 2006 Kolb et al. have observed a capacity increase when blending graphite with a commercially available polysilazane (VL20®). These investigations have revealed that the ceramic SiCN phase prevents the graphite from exfoliating and thus stabilizes electrode material during cycling. The measured capacity was 474 mAh·g<sup>-1</sup> without any fading up to 50th cycle [5].

In the following years several SiCN ceramics and SiCN composites have been investigated regarding to their lithium storage ability.

Studies of Graczyk-Zajac et al. revealed good rate capability for SiCN/graphite composites derived from commercially available polysilazane HTT1800. It was shown that the ceramic matrix enhances the electrode performance at high current rates [6]. Chen et al. and Wilamowska et al. started to focus on producing SiCN composites containing highly disordered carbon derived from divinyl benzene and starch. Introduction of disordered carbon into the composites leads to further increase of reversible capacities to 484 mAh·g<sup>-1</sup> and 570 mAh·g<sup>-1</sup>, respectively [7,8]. Furthermore, significant improvements in electrochemical performances of functionalized PDCs have been reported in literature [9–15] emphasizing benefits of Si-based ceramics. Reinold et al. published results on carbon-rich SiCN ceramics derived from in-house synthesized preceramic polymers reaching reversible capacities of ~640 mAh·g<sup>-1</sup> and outstanding cycling stability [4]. The dependence of electrochemical performance on the pyrolysis temperature of non-porous SiCN ceramics has also been addressed [16].

Within this work, we focus on the influence of the pyrolysis temperature on the lithium storage properties of highly porous carbon-rich SiCN ceramics synthesized at 900 °C, 1100 °C and 1400 °C. The differences in the electrochemical performance of the studied ceramics are rationalized by the increasing organization of the free carbon phase within the SiCN matrix. Hence, the ceramic powders are characterized by means of N<sub>2</sub>-adsorption, X-ray diffraction, Scanning Electron

\* Corresponding author.

E-mail address: [vrankovic@materials.tu-darmstadt.de](mailto:vrankovic@materials.tu-darmstadt.de) (D. Vrankovic).

Microscopy (SEM) and by Raman spectroscopy. Electrochemical studies reveal the excellent electrochemical performance of 900 °C samples with stable delithiation capacities up to  $\sim 550 \text{ mAh}\cdot\text{g}^{-1}$  at  $72 \text{ mA}\cdot\text{g}^{-1}$  current density over  $> 100$  cycles and  $> 200 \text{ mAh}\cdot\text{g}^{-1}$  at  $1890 \text{ mA}\cdot\text{g}^{-1}$ .

## 2. Experimental part

The details of the synthesis of porous carbon-rich SiCN are reported elsewhere [17]. This method allows for producing mesoporous ceramics with total carbon content of  $\sim 50 \text{ wt}\%$ , whereas the carbon content does not change significantly with increase of pyrolysis temperature [18]. The samples were produced by setting the pyrolysis temperature ( $T_{\text{pyr}}$ ) to 900 °C, 1100 °C and 1400 °C.

The carbon content in prepared SiCN samples was analyzed by hot-gas extraction using a Leco-200 carbon analyzer. It amounts 49–50 wt% in 900 and 1100 °C samples, respectively and increases slightly to 54 wt% for 1400 °C due to the carbothermal reduction leading to the loss of nitrogen,  $\text{Si}_3\text{N}_4 + 3\text{C} \rightarrow 3\text{SiC} + 2\text{N}_2$ . The increase of carbon content is however not significant due to the low reaction extent at 1400 °C.

X-ray powder diffraction was performed on the as prepared powders using a STOE STADI P (STOE, Germany) equipped with monochromatic Mo- $K_\alpha$  radiation in flat-sample transmission geometry in the  $2\theta$  range of  $5^\circ$  to  $45^\circ$ .

Micro-Raman spectra of the powder samples were recorded by using a micro-Raman spectrometer Horiba HR800 (Horiba, Japan) using an Ar-Ion laser of wavelength 514.5 nm and a Raman shift range of  $0 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ . For all samples the filters and measuring parameters were kept constant.

Nitrogen ( $\text{N}_2$ ) adsorption was performed at 77 K using an Autosorb-3B (Quantachrome Instruments, USA). The samples were preheated at 150 °C for 24 h under vacuum before the measurements. The  $\text{N}_2$  isotherm at 77 K was used to calculate the specific surface area (SSA) from the linear BET (Brunauer–Emmett–Teller) plots over the relative pressure range of  $0.05 < p/p_0 < 0.3$ . The total pore volume ( $V_t$ ) was determined from the amount of vapor adsorbed at a relative pressure  $p/p_0 \approx 1$  [19].

SEM pictures of pristine and cycled electrodes were taken at a JEOL JSM-7600F Field Emission electron microscope (JEOL, Japan). The cycled electrodes were disassembled from the Swagelok® cell and washed with dimethyl carbonate. The samples were coated with a thin layer of gold using a Quorum Q300T D (Quorum Technologies Ltd., United Kingdom) for 20 s at 30 mA. Imaging was performed at an acceleration voltage of 10 kV with a secondary electron detector.

For electrochemical testing, electrodes were produced by dispersing 85 wt% active material, 5 wt% Carbon Black Super P® (Timcal Ltd., Switzerland) as conduction additive and 10 wt% polyvinylidene fluoride (PVDF, SOLEF Solvay, Germany) as binder, in N-Methyl-2-pyrrolidone (NMP, BASF, Germany). The slurry was printed on a copper foil (10  $\mu\text{m}$ , Copper SE-Cu58 (C103), Schlenk Metallfolien, Germany) with a coating thickness of 100  $\mu\text{m}$ . After drying round electrodes 10 mm in diameter and an average loading of approximately  $2.50 \text{ mg}\cdot\text{cm}^{-2}$  were cut out and dried in glass oven B-585 Drying (Büchi Labortechnik AG, Germany) for 24 h at 80 °C under vacuum.

Electrochemical study was done using Swagelok® type cells with lithium foil (99.9% purity, 0.75 mm thickness, Alfa Aesar, Germany) of 10 mm in diameter as counter electrode, 180  $\mu\text{L}$  of 1 M  $\text{LiPF}_6$  in EC:DMC-1:1 electrolyte (Solvionic, France) and QMA glass fiber filters (Whatman™, United Kingdom) as separator. Measurements were done using VMP-multipotentiostat (Biologic Science Instruments, France) and controlled constant temperature of 25 °C. Cells were cycled by galvanostatic cycling with potential limitation (GCPL) in a potential range of 0.005 V–3 V with a current of  $72 \text{ mA}\cdot\text{g}^{-1}$  for 100 cycles and high current cycling with stepwise increasing currents (rates) of  $74.4 \text{ mA}\cdot\text{g}^{-1}$  (C/5),  $372 \text{ mA}\cdot\text{g}^{-1}$  (C),  $744 \text{ mA}\cdot\text{g}^{-1}$  (2C),  $1860 \text{ mA}\cdot\text{g}^{-1}$  (5C),  $3720 \text{ mA}\cdot\text{g}^{-1}$  (10C).

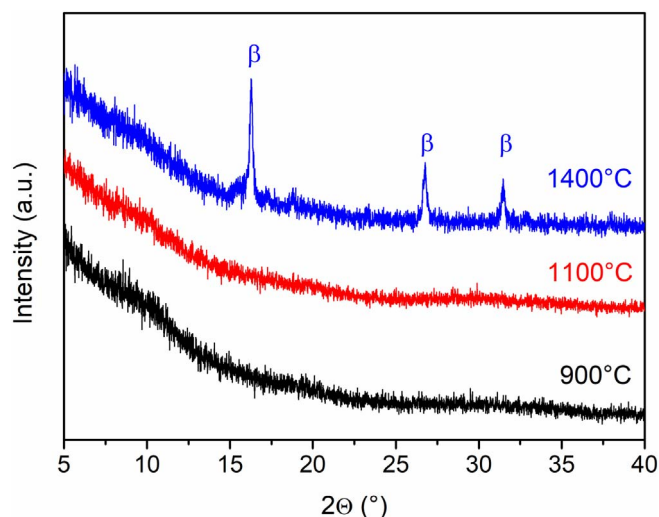


Fig. 1. X-ray diffraction pattern of 900 °C, 1100 °C and 1400 °C samples measured with Mo- $K_\alpha$  source.

## 3. Results and discussion

### 3.1. X-ray diffraction study

The recorded X-ray diffraction patterns depicted in Fig. 1 indicate the highly amorphous nature of the samples pyrolysed at 900 °C and 1100 °C [20]. With increasing the pyrolysis temperature to 1400 °C, three reflexes ( $\beta$  marker) arise at  $2\theta$  angles of  $16.3^\circ$ ,  $26.7^\circ$  and  $31.4^\circ$ . These reflexes are attributed to a SiC-phase formed during carbothermal reduction [21]. Furthermore this onset of crystallization at 1400 °C is in good accordance with the work of Mera et al. who reported crystallization of SiC from poly(phenylvinylsilylcarbodiimide) at around 1400 °C [22].

### 3.2. Nitrogen adsorption

Porosity analysis via  $\text{N}_2$ -adsorption has shown that the specific surface area (SSA) and the total pore volume ( $V_t$ ) decrease with increasing pyrolysis temperature from 900 °C to 1100 °C (Table 1). The steady decrease of SSA and  $V_t$  with increase of pyrolysis temperature is attributed to sintering of small mesopores. In the temperature range of 1100 °C to 1400 °C an additional pore formation is found implying the increase of SSA and  $V_t$ . This increase is related to the reaction of the free carbon phase with the Si-network to the formation of SiC [23].

### 3.3. Electrochemical characterization

Fig. 2a presents the extended cycling performance of porous SiCN ceramics pyrolysed at 900 °C, 1100 °C and 1400 °C, whereas the corresponding coulombic efficiencies are presented in Fig. 2b. The decrease of performance in the first few cycles is attributed to irreversible loss originating from the ongoing decomposition of the electrolyte known as solid electrolyte interface (SEI) and irreversible trapping of Li-ions in the porous structure. Subsequently the sample pyrolysed at 900 °C shows steady increase of capacity up to  $534 \text{ mAh}\cdot\text{g}^{-1}$  due to

Table 1  
Specific surface area and total pore volume measured via  $\text{N}_2$ -adsorption.

Sample	SSA ( $\text{m}^2\cdot\text{g}^{-1}$ )	$V_t$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )
900 °C	169	0.48
1100 °C	104	0.46
1400 °C	446	0.72

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