Lithium containing silazanes as precursors for SiCN:Li ceramics—A potential material for electrochemical applications

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Abstract

Lithium containing silicon carbonitride ceramics (SiCN:Li) were synthesized via precursor-to-ceramic-transformation of Li-containing (poly)silazanes. The precursors were obtained by lithiation of the model compound 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane and of a commercial poly(organosilazane) VL20® with *n*-butyllithium in different molar ratios. According to Raman spectroscopic measurements, lithiation takes place at the NH groups of the molecular organosilazane structure. If the amount of *n*-BuLi exceeds the stoichiometric amount of NH groups, addition of *n*-BuLi at the vinyl groups (attached as substituents at the Si atoms of the silazane) occurs. Thermal analysis coupled with in situ mass spectrometry evidenced the loss of methane and hydrogen as the main gaseous by-products formed during the precursor-to-ceramic-transformation. The ceramization process is completed at $1100\,^{\circ}C$ in argon and yielded Li-containing silicon carbonitride, SiCN:Li. X-ray powder diffraction revealed that the resulting SiCN:Li ceramics were basically amorphous and contained $LiSi_2N_3$ as a crystalline phase with increasing amount of Li. Possible applications of the new SiCN:Li ceramics are seen in the field of Li-ion batteries as alternative anode or solid electrolyte material.
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1. Introduction

Organosilazane polymers are excellent precursors for the formation of silicon carbonitride (SiCN), silicon nitride (Si_3N_4) and silicon carbide (SiC) via alternative processing routes.[1,2]

While preceramic poly(organosilazanes) have been intensively studied in the past, only few papers have reported work on vinyl-substituted cyclotrisilazane as a precursor for SiCN ceramics.[3–8] Besides the study of silicon carbonitride as structural material, the electrical properties of these ternary ceramic systems have also been investigated.[8–11] However, to our knowledge, only one report dealing with the electrical properties of ceramics made from cyclotrisilazane has been published so far.[8] Moreover, polysilazane-derived electrode materials and their potential use in lithium ion batteries has been reported in several patent applications by Dahn et al.[12]

In the present study, we synthesized and investigated novel lithium containing precursors based on 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane and on commercial polysilazane VL20® which yielded SiCN:Li ceramics upon thermolysis at $1100\,^{\circ}C$ in Ar atmosphere.

The precursor-to-ceramic conversion was investigated by simultaneous thermal gravimetric analyses (TGA) coupled with mass spectrometry, Raman spectroscopy, X-ray diffraction (XRD) and elemental analysis. The motivation of the work presented here is related to the chemical resistance and high thermal stability of the SiCN matrix material. Introducing Li into the solid SiCN network can result in novel ceramics suitable for applications as: (i) the anode material; and/or (ii) the Li ion conductor in Li-ion batteries.

2. Experimental procedure

2.1. General comments

All reactions were carried out in purified argon atmosphere using standard Schlenk techniques.[13] The commercial polysilazane VL20® was obtained from KiON (Pennsylvania, USA). 2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane, and *n*-butyllithium solution 2.5 M in *n*-hexane were purchased from

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Aldrich (Milwaukee, USA). All chemicals were used as received without further purification.

2.2. Synthesis of the polymers

The Li-(poly)silazanes were prepared according to the following synthetic route: in a 1 L Schlenk flask equipped with a magnetic stir bar, 10 mL (38 mmol, 1 eq.) of 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane were solved in abs. *n*-hexane and cooled to $-70\,^{\circ}C$. After stirring for 30 min, the *n*-butyllithium solution diluted with additional 100 mL *n*-hexane was added slowly (sample **1**: 45 mL, 113 mmol, 3 eq.; sample **2**: 76 mL, 226 mmol, 6 eq.). After stirring for a further 20 h with warming to room temperature (**1**) or subsequent refluxing in *n*-hexane (**2**) the reaction solution was filtrated. The products were dried at room temperature under reduced pressure (2×10^{-2} mbar), and finally isolated as colorless to light yellow powders. VL20® was lithiated via an analogous synthesis route: 10 mL polysilazane were solved in *n*-hexane and an excess amount of *n*-BuLi was added at $-70\,^{\circ}C$ (sample **3**: 64 mL *n*-BuLi, sample **4**: 132 mL *n*-BuLi). The amount of butyllithium was estimated by approximating the molecular mass of the Si–N units (70 g/mol, according to information obtained from KiON).

2.3. Ceramic conversion process

Pyrolysis experiments of the precursors were carried out in a GERO tube furnace equipped with an internal alumina tube under continuous argon flow. The samples were heated to $1100\,^{\circ}C$, at a rate of $100\,^{\circ}C/min$ and held for 5 h at this temperature. Finally, the samples were cooled down to room temperature at $200\,^{\circ}C/min$.

2.4. Characterization techniques

The reaction products were investigated by Raman spectroscopy. The Raman spectra of the precursors were collected on a Bruker FT Raman Modul FRA 106 equipped with a germanium detector (D 418-S) and a 1064 nm laser excitation source. Raman measurements of the resulting ceramics were performed at the MPI für Festkörperforschung, Stuttgart, Germany, using a LabRam System 010 with a 632 nm HeNe laser (Jobin Yvon). Thermal analyses were performed with a Simultaneous Thermal Analyzer STA 429 (Netzsch, Germany). The gases evolved during pyrolysis were detected with a Balzers QMA 400 mass spectrometer coupled to the STA equipment. TGA experiments were performed at a heating rate of $5\,^{\circ}C/min$ under argon. ^{13}C magic angle spinning (MAS) NMR experiments were carried out using a Bruker ASX 400 spectrometer. To measure the ^{13}C NMR spectrum, a standard cross polarization (CP) pulse sequence was used, where the contact time was 3 ms and, the recycle time was 5 s. The spinning rate was 4 kHz. The chemical compositions of the precursors, as well as the Li content of the ceramics were investigated by Mikrolabor Pascher, Remagen, Germany. The C, N and O content of the ceramics were analyzed by hot gas extraction using a C-Analyzer Leco C-200 and NO-Analyzer Leco TC-436, respectively. X-ray diffraction (XRD) measure-

ments were carried out on a Stoe Stadi P powder diffractometer using Mo Kα1 radiation.

3. Results and discussion

The lithiation reaction of cyclic silazanes with *n*-butyllithium in dry argon atmosphere leads to SiCN:Li preceramic compounds (Eqs. (1)–(3)). In particular, the reactions were performed in *n*-hexane as solvent at reduced temperature or in refluxing *n*-hexane. Precipitation of the resulting lithium salt is observed during the reaction. The obtained products are colorless to light yellow powders sensitive against water and air and show no melting up to $400\,^{\circ}C$.

Products **1** and **2** are formed starting from 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane while compounds **3** and **4** result from the reaction of *n*-BuLi with polysilazane VL20®.

$$(1)$$

$$(2)$$

R = H, Vinyl
R' = Alkyl
n = 1–20

$$(3)$$
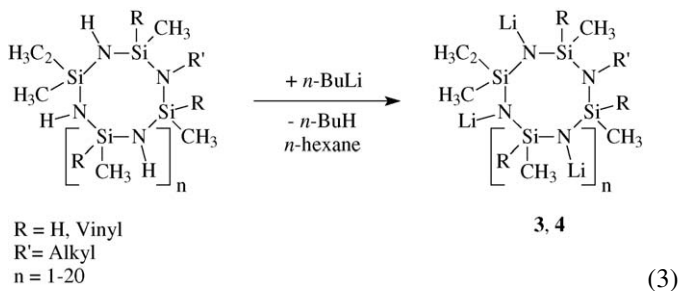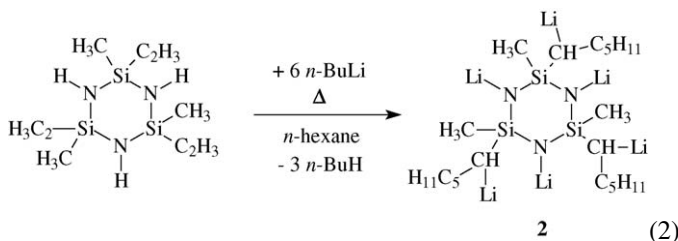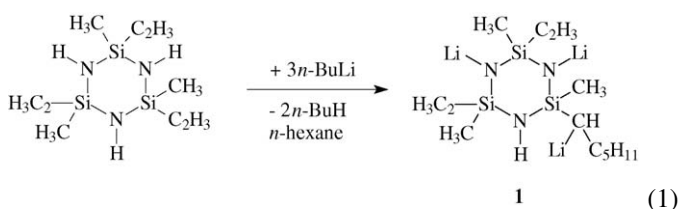
The obtained Li-(poly)silazanes were investigated by elemental analysis. The data of the synthesized products **1–4** are listed in Table 1. It is evident that the analytical results of the synthesized compounds **1** and **2** are in agreement with the expected Si:N:Li ratio. According to reaction Eq. (1), the cyclotrisilazane is lithiated twice at NH groups while the third mole *n*-BuLi is

Table 1
Elemental analysis of SiCN:Li-precursors **1–4**

Precursor	Molecular formula (found)	Molecular formula (calculated)
1	$Si_1C_{4.1}H_{9.2}N_1Li_{1.1}$	$Si_1C_{4.3}H_{9.3}N_1Li_1$
2	$Si_1C_{6.6}H_{15.2}N_1Li_{2.4}$	$Si_1C_7H_{15}N_1Li_2$
3	$Si_1C_{2.1}H_{6.5}N_{1.1}Li_1$	[a]
4	$Si_1C_{5.9}H_{12.6}N_{1.1}Li_{3.4}$	[a]

[a] Calculation not possible due to unknown content of NH and vinyl groups in the commercial polysilazane VL20®.

added at one of the vinyl groups attached to Si. This finding is clearly evidenced by elemental analysis of the C and H content (see Table 1) as well as by ^{13}C MAS-NMR spectroscopy. In the ^{13}C NMR spectrum of sample **1**, chemical shift values due to characteristic $-CH_2$ groups ($\delta = 13, 23,$ and 32 ppm) formed by the addition of *n*-BuLi to vinyl are identified besides the typical chemical shift of vinylic carbon atoms ($\delta = 127$ and 151 ppm). The reaction of one mole cyclotrisilazane with six mole *n*-BuLi results in the complete lithiation of the NH groups as well as in the complete addition of *n*-BuLi to the vinyl groups (reaction Eq. (2)).

In the case of compounds **3** and **4,** derived from polysilazane VL20®, different Si:N:Li ratios can be adjusted by varying the amount of *n*-BuLi according to reaction Eq. (3).

In all SiCN:Li-precursors **1–4**, an oxygen contamination of 1–6 wt.% was analyzed which is ascribed to manipulation of the samples in air and is also found in the pyrolyzed products (see below). Similar results have been reported for as synthesized SiCN ceramics by other authors.[14–16]

Raman spectra of the SiCN:Li-precursors **1–4** as shown in Fig. 1 support the concept that the lithiation reaction proceeds according to reaction Eqs. (1)–(3). Compared to the spectra of the starting compounds, no absorption bands at around $3500\ cm^{-1}$ that could be assigned to N—H vibrations are found in the lithiated products. This result indicates lithiation at the nitrogen atom. The remaining N—H group in compound **1** could, however, not be resolved in the Raman spectrum. In addition, the Raman spectrum of precursor **1** contains typical modes corresponding to the presence of vinyl groups at around 1400, 1600 and beyond $3000\ cm^{-1}$ which are not found in the spectra of compounds **2**, **3** and **4** (see Fig. 1a and b). The absence of vinyl vibrations in sample **2** confirms the addition of *n*-BuLi to the vinyl group. Moreover, hydrosilylation reaction of Si—H with vinyl groups has to be taken into account in the case of compounds **3** and **4**.[16]

Further characteristic bands are found between 100 and $1500\ cm^{-1}$ as well as between 2800 and $3000\ cm^{-1}$. The former vibrations are assigned to Si—N—Si, Si—N, and Si—C while the latter broad absorption corresponds to aliphatic C—H bonds (stretching vibrations of CH_3 groups).

The thermal behavior of the reaction products was studied between room temperature and $1100\ ^{\circ}C$ by thermal gravimetric analysis (TGA). Gaseous decomposition products were analyzed by in situ mass spectrometry. TGA/MS analyses show that the major weight loss for all precursors occurs between ~200 and $600\ ^{\circ}C$ (see Fig. 2). Comparing the ceramic yields between compounds **1** and **2** and compounds **3** and **4** indicates that the weight loss during thermolysis is related to the Li content of the precursor. An increasing Li content results in decreasing ceramic yield: sample **1**: 78%, sample **2**: 68%, sample **3**: 83%, sample **4**: 63%.

As can be seen from Fig. 2 precursors **1**, **3** and **2**, **4** show nearly the same thermal behavior. Precursors **1** and **3** reveal the first and very low weight loss step (~1%) between room temperature and $150\ ^{\circ}C$ corresponding to the loss of residual solvent (*n*-hexane; $m/z = 86$). The second and main weight loss step occurs between 200 and $550\ ^{\circ}C$ (**1**: -21.4%; **3**: -17.6%) and is mainly related to the evaporation of hydrogen ($m/z = 2$) and methane ($m/z = 16$). Precursors **2** and **4** show three weight loss steps. The first step between room temperature and $150\ ^{\circ}C$
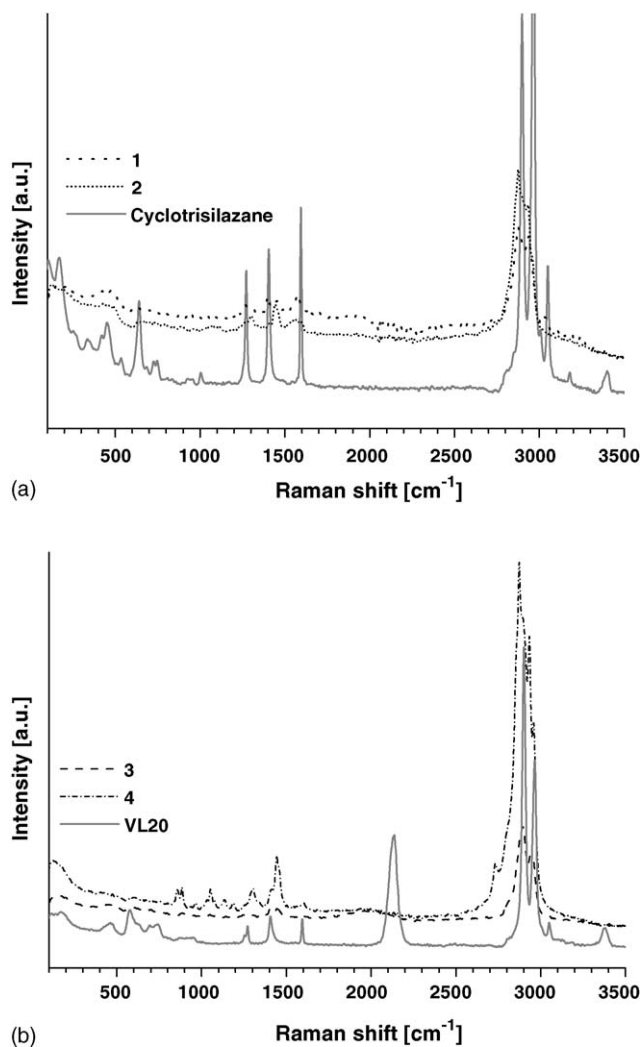

(a)

(b)

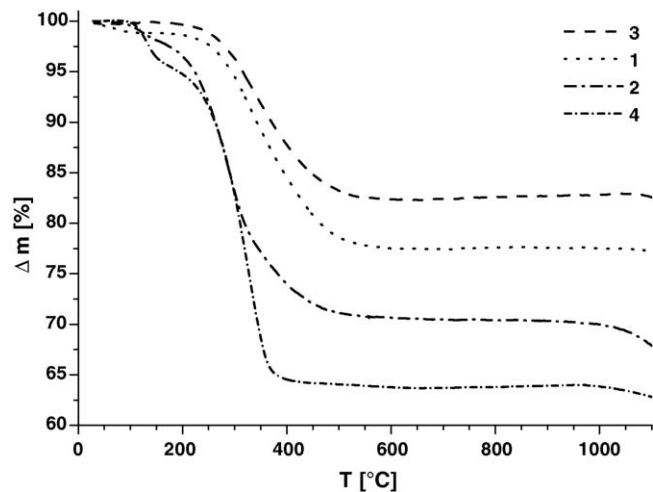Fig. 1. Raman spectra of the precursors **1**, **2** (a), **3** and **4** (b).

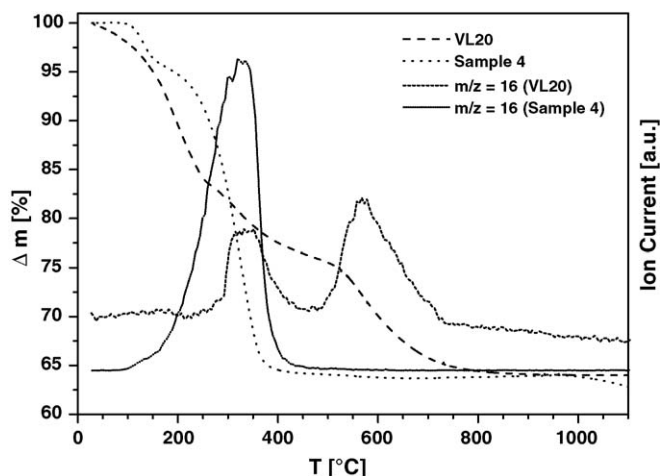Fig. 2. Thermal gravimetric analysis (TGA) of precursor **1–4**.

Fig. 3. TGA/MS of polysilazane VL20® and of the lithiated polymer **4** for comparison. To proof the out gassing of methane and ammonia the mass $m/z = 16$ is depicted, other fragments are not shown for clarity.

amounts to approximately 2 wt.% and is again due to the loss of residual solvent. The next step takes place between 150 and 500 °C. In this temperature range also hydrogen and methane are identified. At temperatures above 1000 °C out-gassing of SiO ($m/z = 44$) and CO ($m/z = 28$) is analyzed.

In general for organosilazanes, the evaporation of methane starts at temperatures of about 400–500 °C.[14–17] It is remarkable that the lithiated polysilazanes give off methane at a significantly lower temperature. The first loss of methane ($m/z = 16$) was detected at around 200 °C as is shown for sample **4** in Fig. 3. In the case of Li-free polysilazane VL20®, the appearance of the mass $m/z = 16$ identified between 300 and 400 °C is associated with the loss of ammonia instead of methane and is due to progressive cross linking via polycondensation. The loss of methane in VL20® is found between 500 and 700 °C. To distinguish between ammonia and methane, we used the temperature dependent evolution of other fragments. For methane we also analyzed species with $m/z = 13$ and 12 besides $m/z = 16$ while for ammonia the mass $m/z = 17$ is detected in addition to $m/z = 16$.

Cross-linking of the compounds **1–4** occurs via polycondensation as discussed elsewhere.[17] The precursor-to-ceramic conversion process was completed at 600 °C in inert argon atmosphere. The loss of CH_4 and hydrocarbons C_nH_m during polymer decomposition significantly reduces the amount of carbon in the final ceramic product obtained at 1100 °C. The overall carbon content is an important feature of the material since it can control the electrochemical behavior of the SiCN:Li ceramics.

The Raman spectra of the formed SiCN:Li ceramics show vibrations located between 1325 and 1341 and 1570 and 1581 cm^{-1} which are characteristic for the two main bands of diamond-like sp^3 (D band) entities and amorphous or graphite-like sp^2-carbon (G band) (see Fig. 4). This finding clearly indicates that amorphous or graphite-like carbon has been separated from the SiCN:Li matrix.

Compositional changes associated with the precursor-to-ceramic transformation were detected by elemental bulk analysis. The results show that, compared to the starting materials, the carbon to nitrogen ratio and the Li content decrease in the
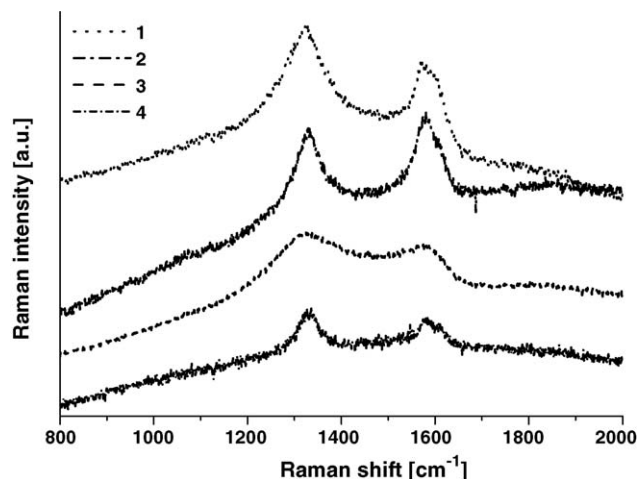

Fig. 4. Raman spectra of the SiCN:Li ceramics **1–4** synthesized from compounds **1–4** at 1100 °C in Ar.

ceramics derived from compounds **1–4** due to the loss of Li and C during thermolysis. The following C:N:O and Li contents (wt.%) were determined: ceramic **1**: C:N:O = 40.7:13.2:1.6, Li = 4.6; ceramic **2**: C:N:O = 49.2:9.3:4.3, Li = 4.9; ceramic **3**: C:N:O = 22.9:16.8:0.6, Li = 7.2; ceramic **4**: C:N:O = 31.9:8.6:3.8, Li = 9.9.

Crystallization and phase separation induced by annealing of the ceramized samples at 1100 °C for 5 h in Ar were determined by means of X-ray powder diffraction. Amorphous SiCN ceramics obtained from cyclo(organosilazane) as well as from poly(organosilazane) start to crystallize at 1450 °C.[7] In contrast, our lithium containing ceramics derived from the preceramic compounds **1–4** already reveal crystallinity at 1100 °C (Fig. 5). However, the diffraction pattern of sample **1** shows a lower amount of crystalline phases compared to sample **2** derived from the same starting material. In addition to the amorphous matrix, both lithium silicon nitride LiSi$_2$N$_3$ and graphite are analyzed as crystalline phases, exclusively. A discussion of the different crystallization behavior between samples **1** and **2–4** can be directed to the elemental composition. But no systematic
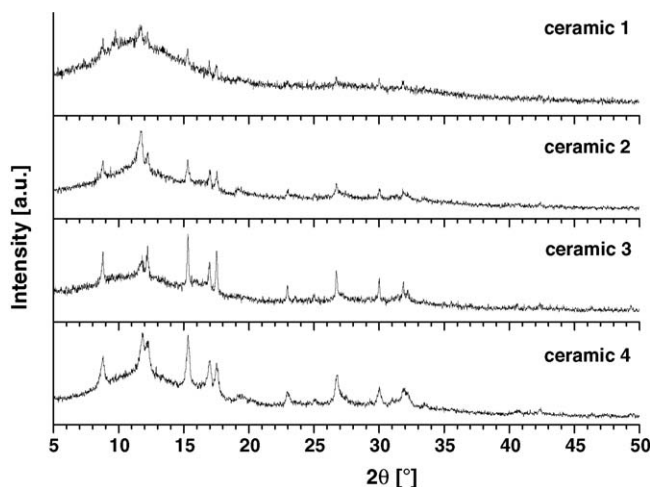

Fig. 5. X-ray powder diffractograms of SiCN:Li ceramics derived from precursor **1–4**.

influence of the Si:C:N:Li ratio as well as of the role of the oxygen contamination on the crystallization behavior can be derived from the present analytical data.

4. Summary

Novel lithium containing molecular Si–N compounds were synthesized via lithiation of organosilazanes. Thermolysis of the Si–N precursors at 1100 °C in Ar atmosphere results in the formation of novel SiCN:Li ceramic compositions.

Raman spectroscopy indicates that lithiation preferentially occurs at the NH groups of the organosilazane molecule. With increasing amount of n-BuLi, addition of butyllithium at vinyl groups attached to Si atoms also takes place.

Thermal analysis coupled with mass spectrometry was carried out to characterize the ceramization process resulting in SiCN:Li ceramics. TGA/MS shows that the major weight loss in all precursors occurs between 200 and 550 °C and is mainly accompanied by the evolution of ammonia due to polycondensation and hydrogen, and methane due to decomposition. It was found that the ceramic yield decreases with increasing lithium content of the precursor.

Elemental analyses of the ceramic products show that the silicon to nitrogen ratio remains unchanged in the ceramic, while the Si:Li and Si:C ratios increase. X-ray powder diffractometry of the synthesized SiCN:Li ceramics exhibits the presence of amorphous and crystalline phases formed at 1100 °C. Lithium silicon nitride and graphite are identified as crystalline phases. Carbon is found in the form of an amorphous or graphite-like structure as can be also seen from the Raman spectra.

Possible applications of the novel lithium containing SiCN ceramics can be expected in the field of Li-ion batteries as anode material and/or Li-ion conductor. Studies related to the electrochemical properties of the SiCN:Li ceramics are presently under investigation and will be reported elsewhere.

Acknowledgements

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