# Silicon Oxycarbide (SiOC) Ceramic Materials as Anodes for Lithium Ion Batteries

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## Introduction

In this work we present correlation between the electrochemical performance of silicon oxycarbides (SiOCs) and their chemical composition and microstructural features. Different SiOC ceramics were prepared by pyrolysis (1000-1300 °C, Ar atmosphere) of various polysiloxanes. These preceramic polymers were synthesized using the sol-gel method. Sol-gel synthesis is a powerful tool for tailoring composition and structure of the final ceramic product. Three alkoxysilanes containing different organic group directly attached to the silicon (R-Si, R=phenyl, vinyl, methyl) were used for sol-gel synthesis of polysiloxanes. The precursors (R-Si-(OC$_2$H$_5$)$_3$) were mixed in different molar ratio in order to investigate the influence of the gels' chemical constitution on the composition and the nano-structure of the final ceramic material. The goal of the synthesis was to achieve optimal composition of the polysiloxanes in order to get carbon-rich silicon oxycarbides. The free carbon phase improves conductivity and provides a main source of lithium storage capacity [1]. However, capacity does not depend linearly with increasing carbon content [2]. Other essential factors influencing reversible capacity are nano-structure and porosity of SiOCs [1-3].

## Sol-gel synthesis

**Precursors:**

Phenyltriethoxysilane
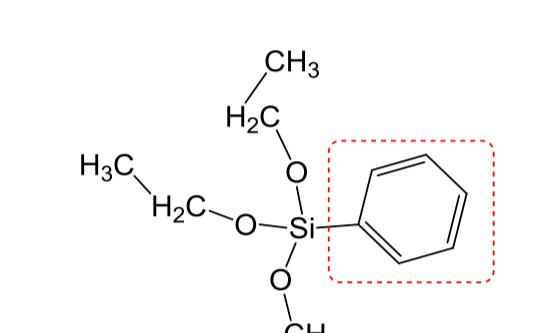
Methyltriethoxysilane
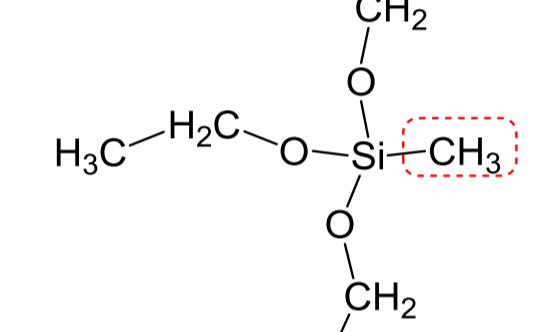
Vinyltriethoxysilane

EtOH 70-85 °C
Hydrolysis and condensation

**Sol:**

Gelation → **Wet gel**

Drying: up to 120 °C, in air → **Xerogel**

Pyrolysis: 1000 °C, 1300 °C, Ar atmosphere C → **Ceramic**

**Hydrolysis of ethoxy groups:**
Si-OCH$_2$CH$_3$+H$_2$O→Si-OH+CH$_3$CH$_2$OH

**Condensation:**
Si-OH + HO-Si → Si-O-Si + H$_2$O
Si–OCH$_2$CH$_3$ + HO–Si → Si–O–Si + CH$_3$CH$_2$OH
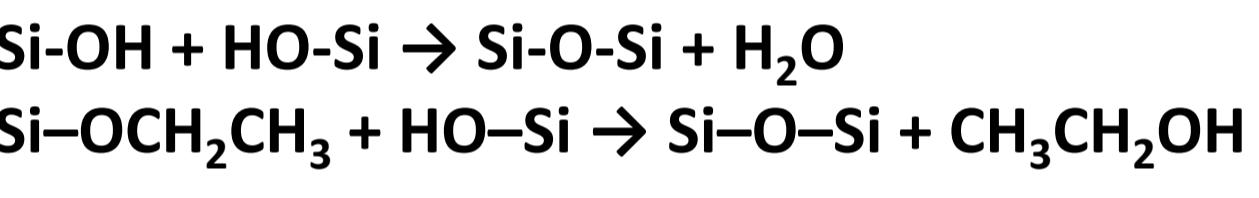
The reactions lead to three dimensional silica network linked with -Si-O-Si- bonds. Organic functional groups (Methyl, Vinyl, Phenyl) do not udergo hydrolysis reaction and after gelation they are fixed to sillica backbone.

## Characterization

Table 1. Results of elemental analysis of the investigated SiOC materials.

| Material | C | O | Si[*] | C$_{free}$ |
|---|---|---|---|---|
| | wt% | | | |
| PhTES | 39.6 | 29.1 | 31.3 | 37.2 |
| PhTES:MTES 2:1 | 30.3 | 30.9 | 38.9 | 25.3 |
| PhTES:MTES 1:1 | 25.9 | 32.4 | 41.7 | 20.2 |
| PhTES:MTES 1:2 | 25.4 | 32.2 | 42.4 | 19.4 |
| PhTES:VTES 2:1 | 38.5 | 31.6 | 29.9 | 37.5 |
| PhTES:VTES 1:1 | 38.5 | 26.2 | 35.3 | 33.3 |
| PhTES:VTES 1:2 | 38.0 | 27.6 | 34.4 | 33.7 |
| VTES | 22.9 | 36.8 | 40.3 | 19.5 |
| VTES:MTES 3:1 | 23.7 | 32.0 | 44.3 | 16.7 |
| VTES:MTES 2:1 | 23.2 | 33.3 | 43.5 | 17.1 |
| MTES[**] | 13.3 | 41.2 | 45.5 | 9.4 |

[*] calculated as a difference to 100 %
[**] From ref. [3], Si, C – analysed elements, O – calculated as a difference to 100%

Table 2. $^{29}$Si MAS-NMR characterization of investigated SiOC samples.

| Sample | Pyrolysis temp. [ C] | Si site [%] | | | | |
|---|---|---|---|---|---|---|
| | | SiO$_4$ | SiO$_3$C | SiO$_2$C$_2$ | SiOC$_3$ | SiC$_4$ |
| PhTES | 1000 °C | 76 | 16.4 | 7.6 | - | - |
| PhTES:MTES 2:1 | 1000 °C | 61.1 | 23.7 | 12.5 | 2.7 | - |
| PhTES:MTES 1:1 | 1000 °C | 59.2 | 24.7 | 12.1 | 4.1 | - |
| PhTES:MTES 1:2 | 1000 °C | 54.3 | 27.7 | 11.2 | 6.8 | - |
| PhTES:VTES 2:1 | 1000 °C | 53.4 | 24.3 | 18.2 | - | 4.1 |
| PhTES:VTES 2:1 | 1300 °C | 91.5 | 1.4 | 1.9 | - | 5.2 |
| PhTES:VTES 1:1 | 1000 °C | 54.0 | 27.5 | 16.0 | 1,5 | 1.0 |
| PhTES:VTES 1:2 | 1000 °C | 51.2 | 27.0 | 14.3 | - | 7.5 |
| VTES | 1000 °C | 86.6 | 13.4 | - | - | - |
| VTES:MTES 3:1 | 1000 °C | 56.7 | 31.8 | 10.1 | - | 1.4 |
| VTES:MTES 2:1 | 1000 °C | 53.4 | 33.3 | 13.3 | - | - |
| MTES | 1000 °C | 56 | 30 | 9 | - | 5 |
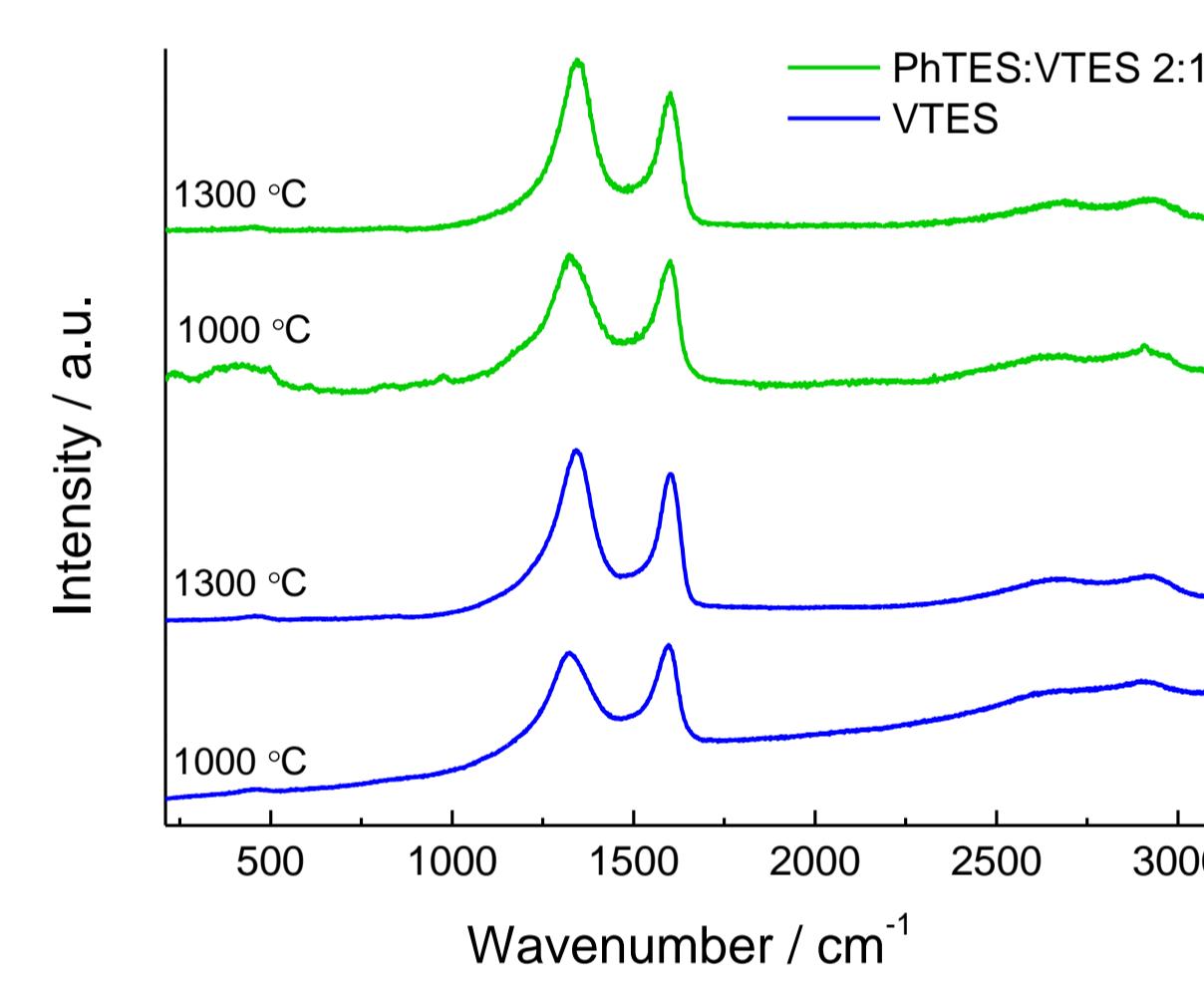


Fig. 1. Raman spectra of chosen SiOC ceramic samples.

Table 3. Location of D and G peaks in Raman Spectra of analyzed samples, intensity ratio of these peaks and calculated average carbon cluster size $L_a$ for materials pyrolyzed at various temperatures

| | Pyrolysis temp. | D [cm$^{-1}$] | G [cm$^{-1}$] | I$_D$/I$_G$ | L$_a$ / Å |
|---|---|---|---|---|---|
| PhTES:VTES 2:1 | 1000 °C | 1325 | 1594 | 1.04 | 13.7 |
| PhTES:VTES 2:1 | 1300 °C | 1343 | 1601 | 1.23 | 14.9 |
| VTES | 1000 °C | 1325 | 1596 | 0.94 | 13.1 |
| VTES | 1300 °C | 1342 | 1603 | 1.16 | 14.5 |

## Electrochemical performance

**Composition of the electrodes**: 85 wt% of active material, 10 wt% of Carbon Black and 5 wt% of PVDF /NMP

**Electrochemical measurements**: two electrode Swagelok® cell; Li foil as counter and reference electrode; electrolyte: 1 M LiPF$_6$ in EC:DMC (1:1); separator: QMA Whatman™. Galvanostatic cycling performed between 3.0 and 0.005 V at different current rates, C=D (C/20=18.6 mA·g$^{-1}$, C/10=37.2 mA·g$^{-1}$, C/5=74,4 mA·g$^{-1}$, C/2=186 mA·g$^{-1}$, C=372 mA·g$^{-1}$, 2C=744 mA·g$^{-1}$).
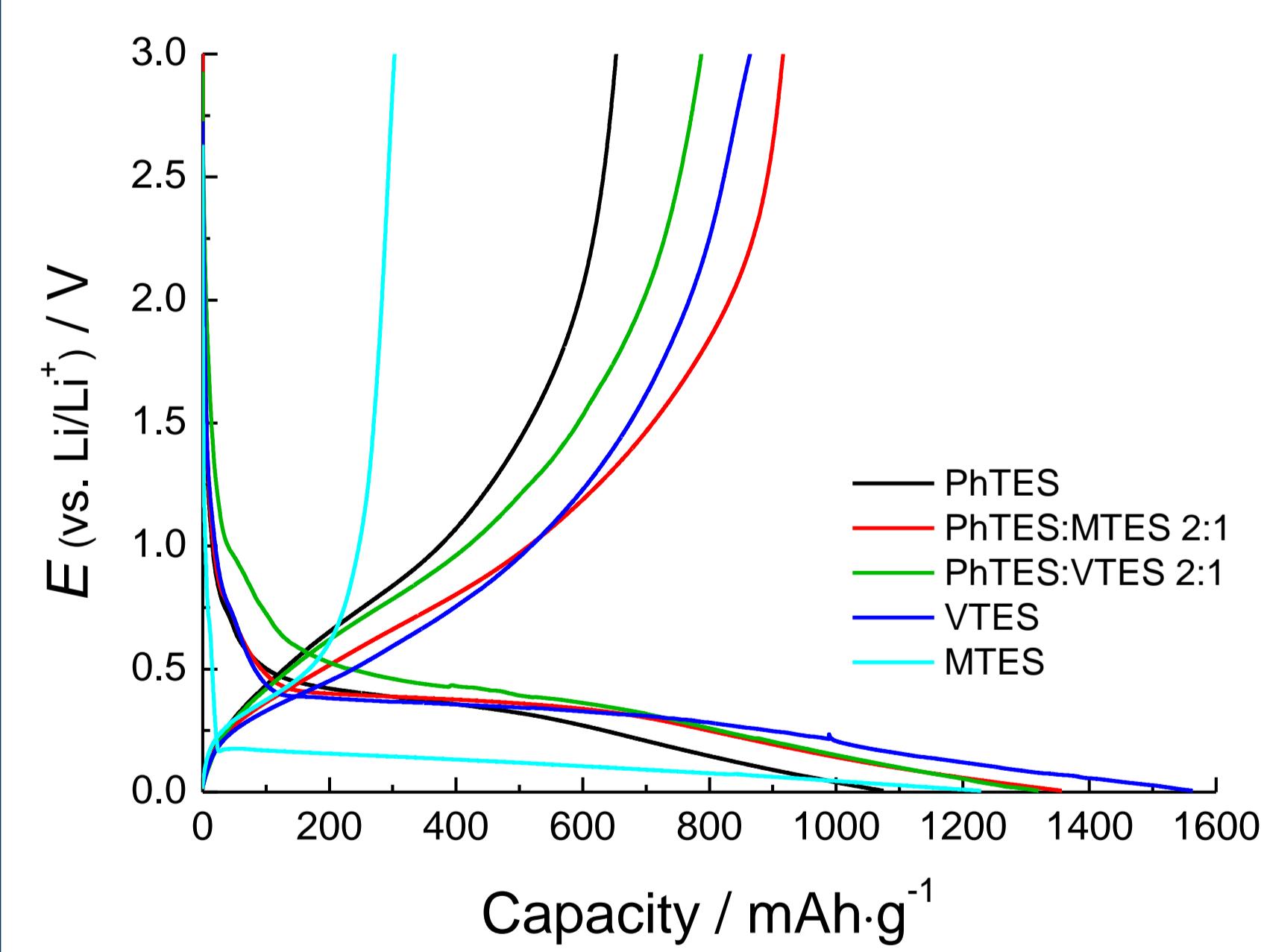


Fig. 2. First lithiation/delithiation cycle of SiOC electrodes; samples pyrolyzed at 1000 °C.
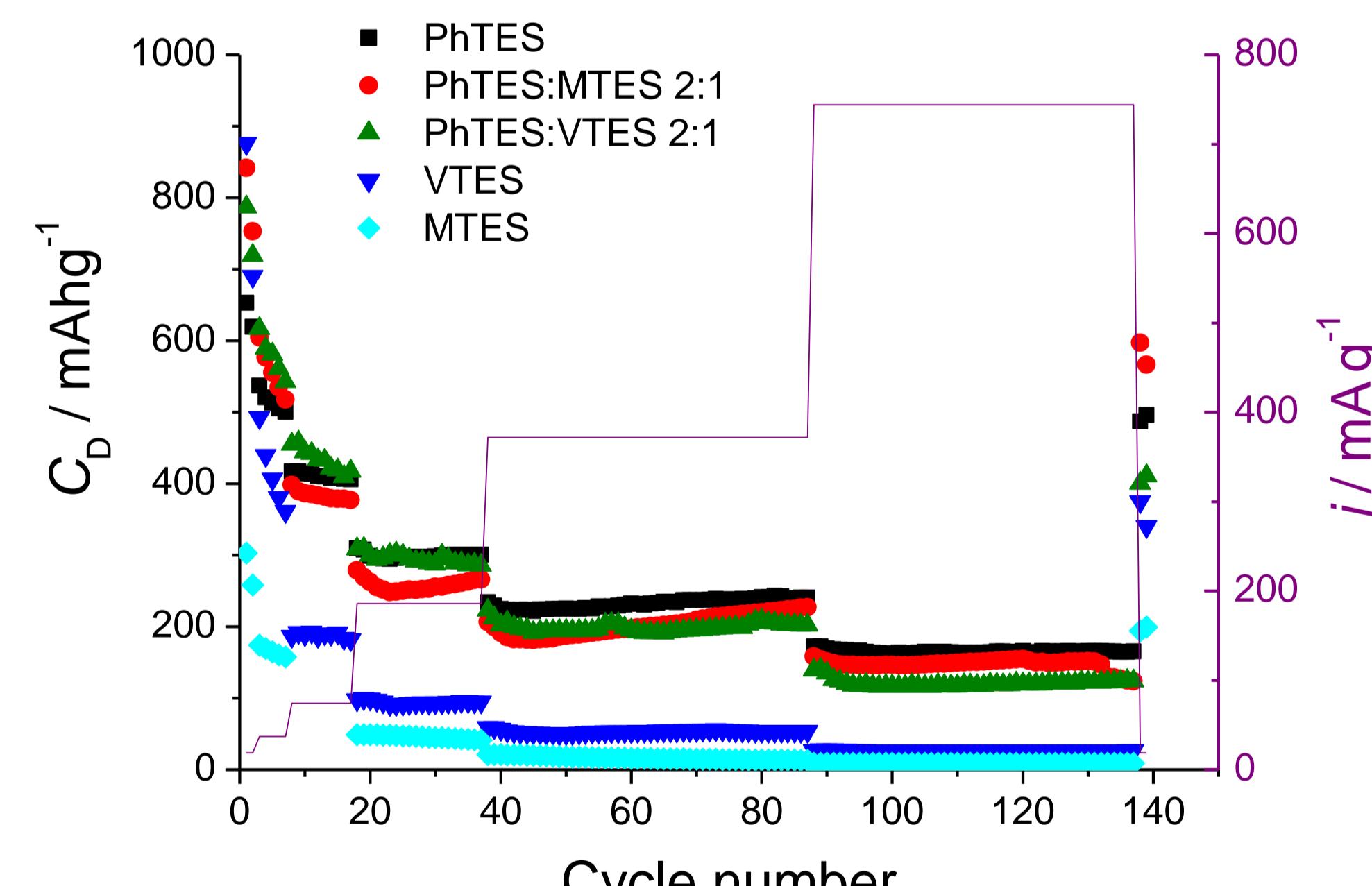


Fig. 3. Discharge capacity vs. cycle number of SiOC electrodes recorded at different current rates; samples pyrolyzed at 1000 °C.
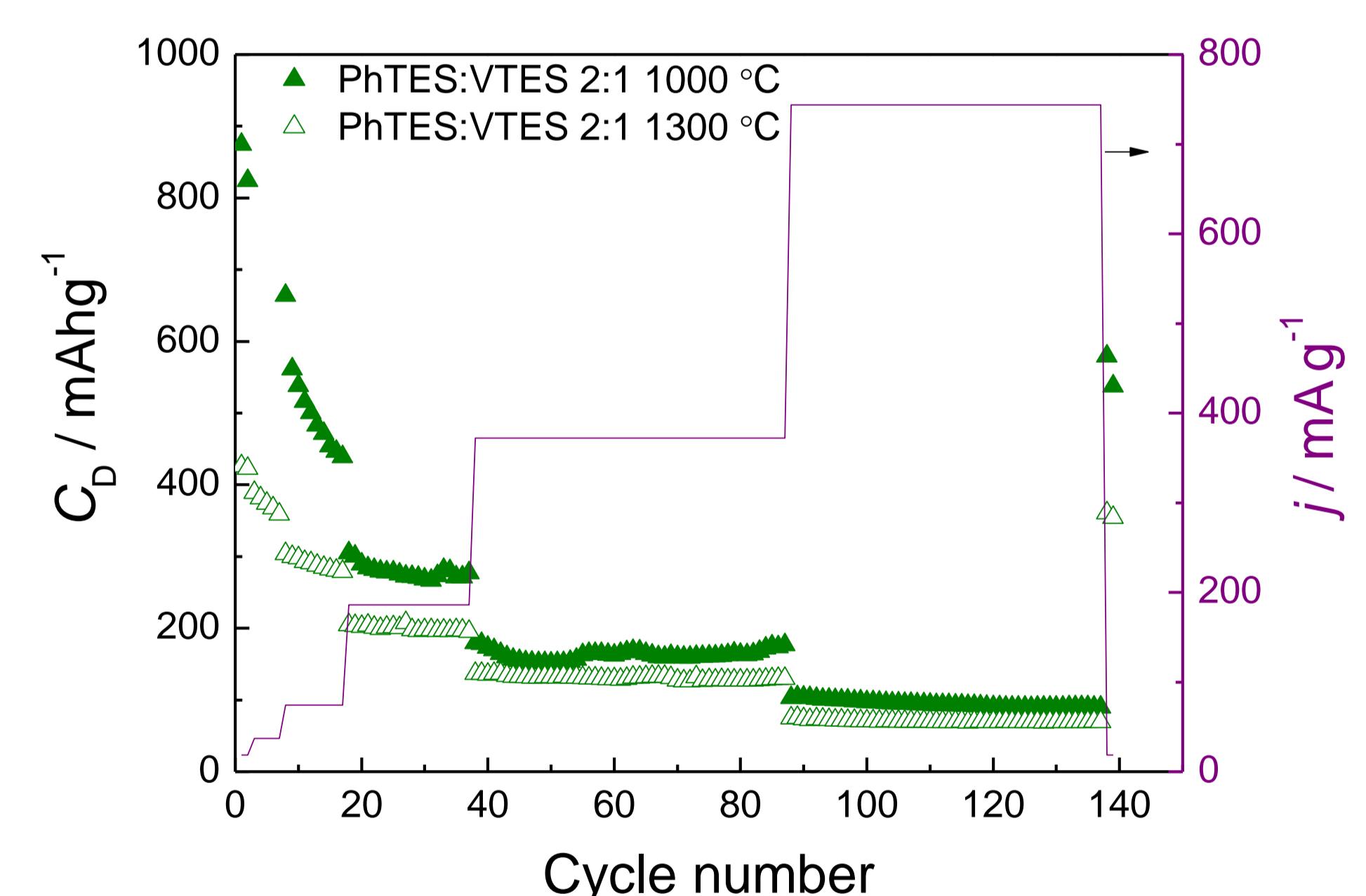


Fig. 4. Discharge capacity vs. cycle number of PhTES:VTES 2:1 sample pyrolyzed at different temperatures

Table 3. Comparison of irreversible capacities $C_{irrev}$ and average discharge capacities $C_D$ of the SiOC electrodes obtained at different current rates.

| Material | 1$^{st}$ cycle $C_D$ / mAh·g$^{-1}$ | | 140$^{th}$ cycle | Average discharge capacity $C_D$ / mAh·g$^{-1}$ | | |
|---|---|---|---|---|---|---|
| | C$_{irrev}$ | C/20 | C/20 | C/2 | C | 2C |
| PhTES | 570 | 721 | 588 | 327 | 257 | 148 |
| PhTES:MTES 2:1 | 440 | 916 | 649 | 384 | 237 | 132 |
| PhTES:VTES 2:1 | 533 | 787 | 411 | 295 | 199 | 121 |
| VTES | 763 | 751 | 340 | 94 | 53 | 26 |
| MTES | 926 | 303 | 199 | 46 | 16 | 9 |

## Summary

➢ Silicon oxycarbides of controlled composition is obtained by selecting suitable starting precursors. The amount of phenyl group in the starting precursors enhances the free carbon content in the final SiOC ceramic.

➢ Pyrolysis at 1000 °C leads to amorphous ceramics.

➢ Elevated pyrolysis temperature (>1300°C) leads to phase separation into SiC and SiO$_2$ → diminishing Li storage activity.

➢ Poor electrochemical performance was observed for samples with low carbon content.

➢ High carbon SiOCs exhibit significant capacity and enhanced cycling stability. 80% of the initial capacity is recovered at a slow rate of C/20 after 140 cycles of continuous charging-discharging with increasing current rate.

➢ No linear dependence of the amount of free carbon phase on the samples electrochemical performance has been found.

## References

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