Carbon-rich silicon oxycarbide (SiOC) – A promising anode material

Recent findings related to microstructural, electrochemical and electroanalytical characterization

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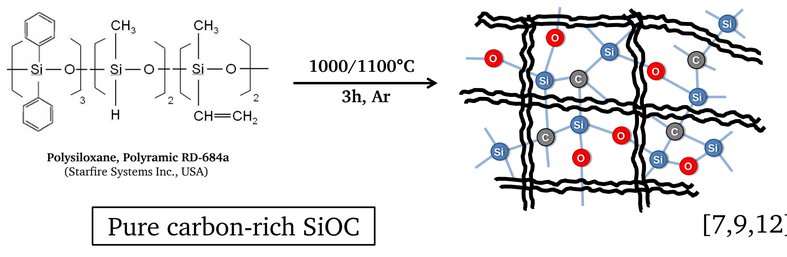
TECHNISCHE UNIVERSITÄT DARMSTADT

Project A4

Motivation

The electrochemical properties of silicon oxycarbide ceramics (SiOC), in view of application as anode material for Li-ion batteries, were first studied in the middle of the 1990's by Dahn et al.. Since that time SiOC compounds with various chemical compositions have been examined and stoichiometries with an exceptionally high content of free carbon were identified as perspective anode materials, with respect to gravimetric capacity, rate capability and cycling behavior.

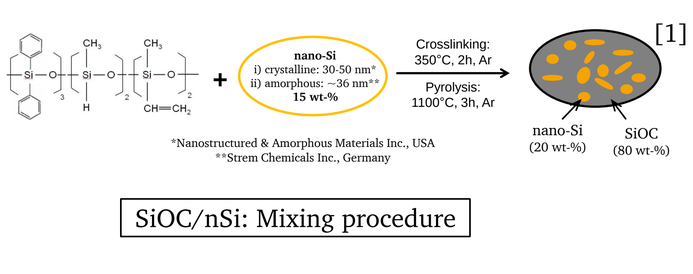
Within the SFB 595/A4, a comprehensive work on the characterization of carbon-rich SiOC derived from commercially available and therefore inexpensive and well-reproducible polyorganosiloxane *RD-684a* (Starfire Systems Inc., USA) was accomplished. It includes profound i) microstructural and chemical, ii) electrochemical and iii) electroanalytical analysis of the ceramic.



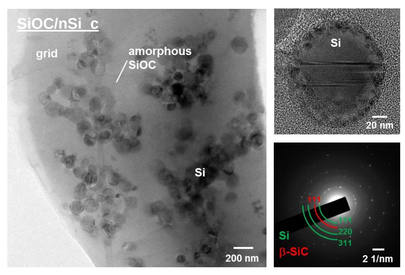
Polysiloxane, Polyramic RD-684a (Starfire Systems Inc., USA)

Pure carbon-rich SiOC [7,9,12]

In a further step, the incorporation of additional electrochemically active, Li-alloy forming elements (Si, Sn) intothe SiOC microstructure was addressed.

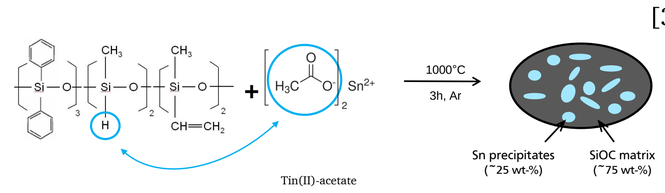


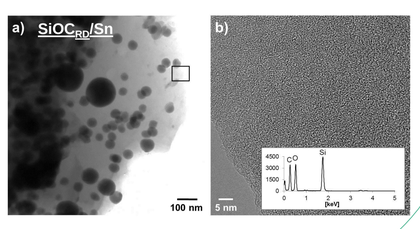
[1]



SiOC/nSi: Mixing procedure

[3]





SiOC/Sn: Chemical modification

Publications last funding period

[1] J. Kaspar, M. Graczyk-Zajac, S. Lauterbach, H.-J. Kleebe, R. Riedel, J. Power Sources, 269 (2014) 164-172.
[2] V.S. Pradeep, M. Graczyk-Zajac, M. Wilamowska, R. Riedel, G.D. Soraru, Solid State Ionics, 262 (2014) 22-24.
[3] Y.M. Nikolaenko, Y.E. Kuzovlev, Y.V. Medvedev, N.I. Mezin, C. Fasel, A. Gurlo, L. Schlicker, T.J.M. Bayer, Y.A. Genenko, J. Appl. Phys., 116(4) (2014) 043704.
[4] J. Kaspar, C. Terzioglu, E. Ionescu, M. Graczyk-Zajac, S. Hapis, H.-J. Kleebe, R. Riedel, Adv. Funct. Mater., 24(26) (2014) 4097-4104.
[5] M. Wilamowska, V.S. Pradeep, M. Graczyk-Zajac, R. Riedel, G.D. Soraru, Solid State Ionics, 260 (2014) 94-100.
[6] S.-H. Baek, L.M. Reinold, M. Graczyk-Zajac, R. Riedel, R. F. Hammerath, B. Büchner, H.-J. Grafe, J. Power Sources, 253 (2014) 342-348.
[7] V.S. Pradeep, M. Graczyk-Zajac, R. Riedel, G.D. Soraru, Electrochim. Acta, 119 (2014) 78-85.
[8] J. Kaspar, M. Graczyk-Zajac, R. Riedel, Electrochim. Acta, 115 (2014) 665-670.
[9] M. Wilamowska, M. Graczyk-Zajac, R. Riedel, J. Power Sources, 244 (2013) 80-86.
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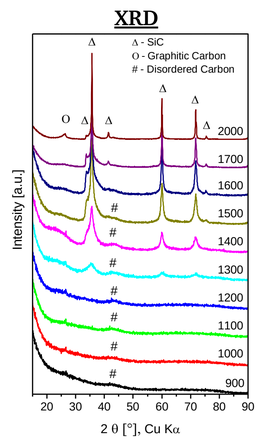
[12] L.M. Reinold, M. Graczyk-Zajac, Y. Gao, G. Mera, R. Riedel, J. Power Sources, 236 (2013) 224-229.
[13] J. Kaspar, M. Graczyk-Zajac, R. Riedel, Solid State Ionics, 225 (2012) 527–531.
[14] M. Graczyk-Zajac, L. Toma, C. Fasel, R. Riedel, Solid States Ionics, 225 (2012) 522–526.
[15] P. Dibandjo, M. Graczyk-Zajac, R. Riedel, V.S. Pradeep, G.D. Soraru, J. Eur. Ceram. Soc., 32(10) (2012) 2495–2503.
[16] M. Graczyk-Zajac, C. Fasel, R. Riedel, J. Power Sources, 196(15) (2011) 6412-6418.
[17] M. Graczyk-Zając, A.M. Lazar, D. Chaumont, M. Sacilotti, R. Riedel, ECS Trans. 35(34) (2011) 207-213.
[18] L.M. Reinold, M. Graczyk-Zajac, C. Fasel, R. Riedel, ECS Trans. 35(34) (2011) 37-44.
[19] J. Kaspar, G. Mera, A. Nowak, M. Graczyk-Zajac, R. Riedel, Electrochimica Acta, 56(1) (2010) 174-182.
[20] M. Graczyk-Zajac, G. Mera, J. Kaspar, R. Riedel, J. Eur. Ceram. Soc., 30(15) (2010) 3235-3243.

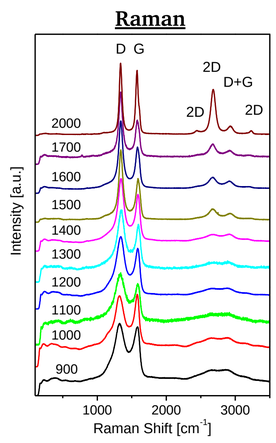
5 Key Publications (2003-2014)

[1] J. Kaspar, C. Terzioglu, E. Ionescu, M. Graczyk-Zajac, S. Hapis, H.-J. Kleebe, R. Riedel, Adv. Funct. Mater., 24(26) (2014) 4097-4104.
[2] S.-H. Baek, L.M. Reinold, M. Graczyk-Zajac, R. Riedel, R. F. Hammerath, B. Büchner, H.-J. Grafe, J. Power Sources, 253 (2014) 342-348.
[3] V.S. Pradeep, M. Graczyk-Zajac, R. Riedel, G.D. Soraru, Electrochim. Acta, 119 (2014) 78-85.
[4] M. Graczyk-Zajac, C. Fasel, R. Riedel, J. Power Sources, 196(15) (2011) 6412-6418.
[5] R. Kolb, C. Fasel, V. Liebau-Kunzmann, R. Riedel, J. Europ. Ceram. Soc., 26 (2006) 3903-390.

Results – Carbon-rich SiOC

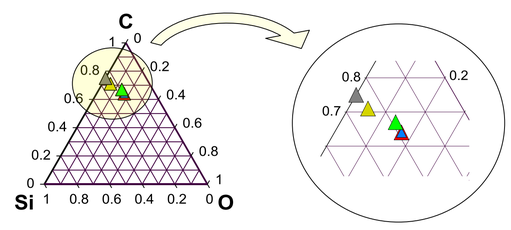
i) Microstructural and Chemical Characterization





Elemental analysis

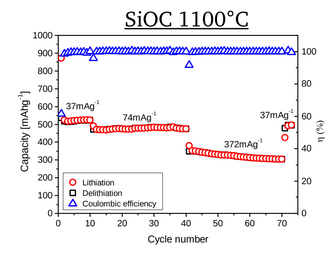
T (°C)	Si (wt-%)	O (wt-%)	C (wt-%)	free C (wt-%)
1100	33.25	17.55	49.20	41.57
1300	33.24	17.65	49.11	41.52
1400	34.43	14.24	51.33	41.95
1500	41.03	5.01	53.96	38.29
2000	43.41	0.04	56.55	38.00

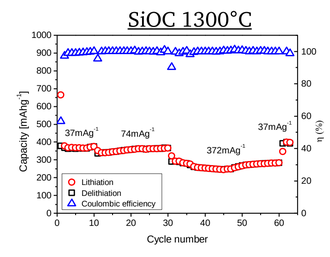


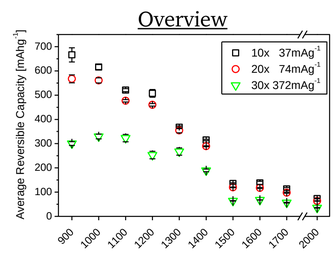
- XRD: Amorphous up to 1200 °C; T > 1200 °C, SiC crystallization; T = 2000°C, formation of graphitic carbon
- Raman: Free carbon phase composed of disordered carbon, I(D) > I(G); increasing carbon organization/graphitization with T ↑, increasing I(2D)
- EA: Diminishing O-content with T ↑; free C-content ~ 40wt-%; similar chemical composition for 1100-1300°C

➢ With increasing T_{pyr} → Increasing carbon organization, partitioning/ decomposition of amorphous Si-O-C network and SiC crystallization

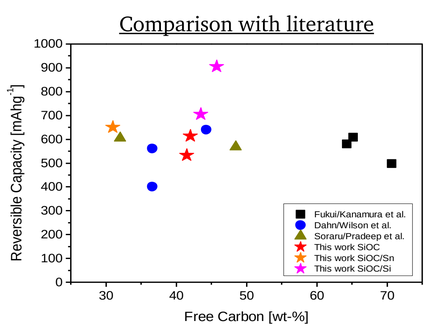
ii) Electrochemical Characterization (GCPL)



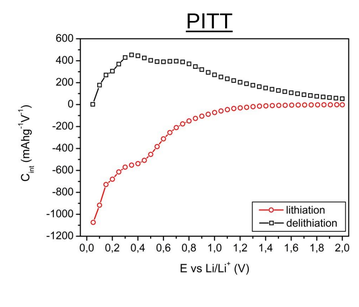


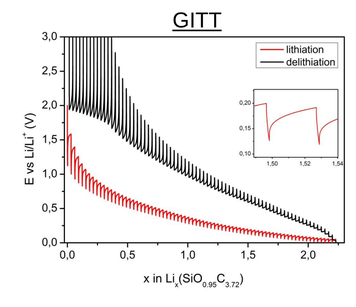


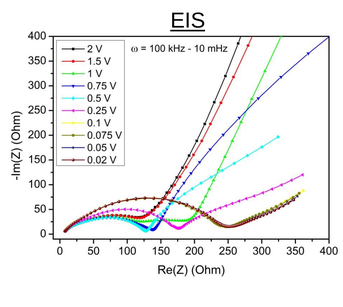
- SiOC 1100 and 1300°C similar chemical composition, but microstructural differences
- Capacity decreases with increasing T_{pyr} ↑
  - ➢ Enhanced carbon organization → Less Li-ion storing sites
  - ➢ Si-O-C partitioning/decomposition → Loss of Li-ion storing sites
  - ➢ Formation of SiC → Electrochemically inactive
- SiOC performance well comparable with literature data, for SiOC/X (X=Si, Sn) further improvement



iii) Electroanalytical Characterization (SiOC 1100°C)



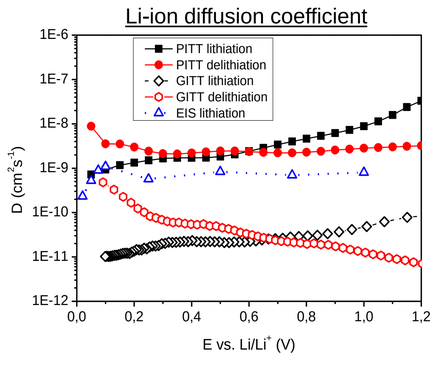




- Estimation of the Li-ion diffusion coefficient as a function of lithiation/delithiation potential by PITT, GITT and EIS

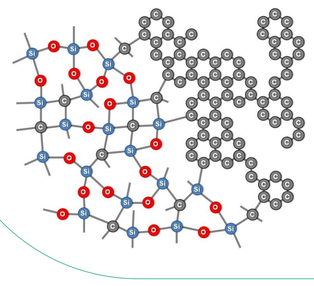
➢ D_{Li^+} amounts 10^{-9} - 10^{-11} cm^2/s; a similar order of magnitude reported for disordered carbons

➢ D_{Li^+} almost independent on the potential; diffusion pathways within the transition regime between the amorphous Si-O-C and free carbon phase

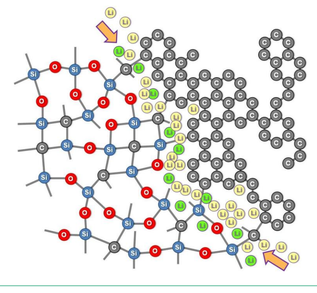


Schematic illustration of the interrelation between i), ii) and iii)

SiOC microstructure



Li-ion insertion, diffusion



Li-ion storage