A4: Novel functional ceramics using anionic substitution in oxidic systems

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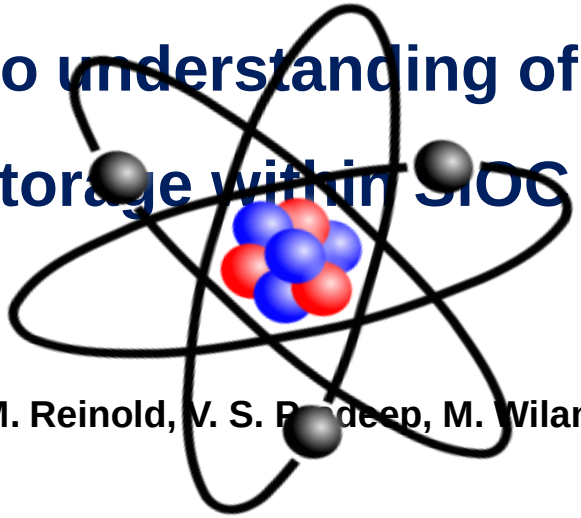
New insights into understanding of irreversible and reversible lithium storage within SiOC and SiCN ceramics



M. Graczyk-Zajac, J. Kaspar, L.M. Reinold, V. S. Pradeep, M. Wilamowska, G.-D. Soraru, R. Riedel

International Symposium on Electrical Fatigue in Functional Materials

Sellin, 15.-18.09.2014

SFB 595 Deutsche Forschungsgemeinschaft DFG

Disperse Feststoffe

Outline

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- **Motivation / Introduction**
  - **Polymer – derived SiOC and SiCN ceramics as battery materials**
  - **Our concept to improve electrode performance**
- **Differences in storing Li-ions in SiCN / SiOC materials:**

➢ **Role of ceramic matrix**

➢ **Role of carbon phase**

- **Summary / Conclusions**

Motivation

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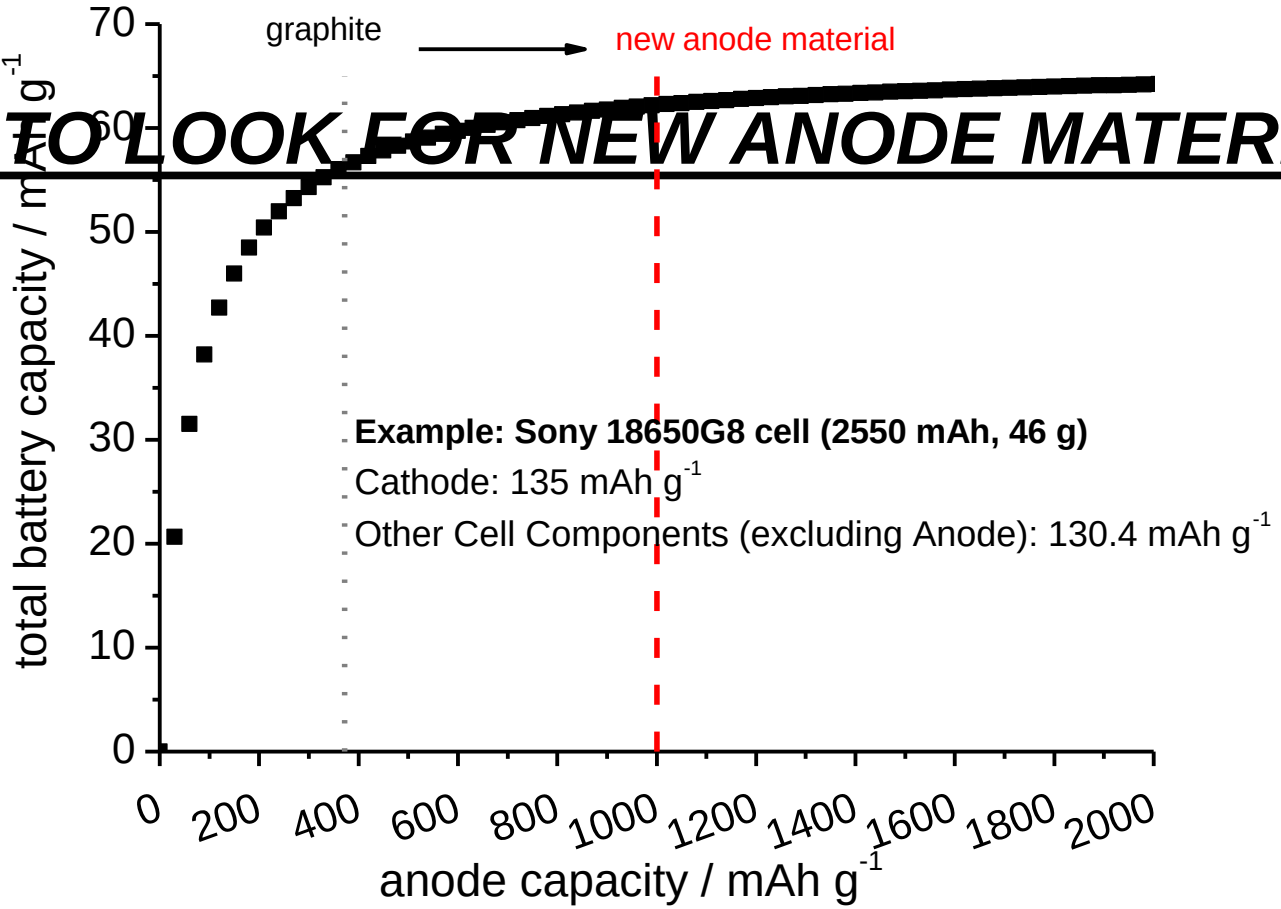
How anode capacity influences the capacity of the battery



WHY TO LOOK FOR NEW ANODE MATERIALS?

Adopted from: Kasavajjula et al. J. Power Sources 2007, 163 ,1003

Our concept for improving anode materials:

Polymer-derived ceramics (PDCs)

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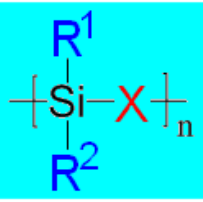
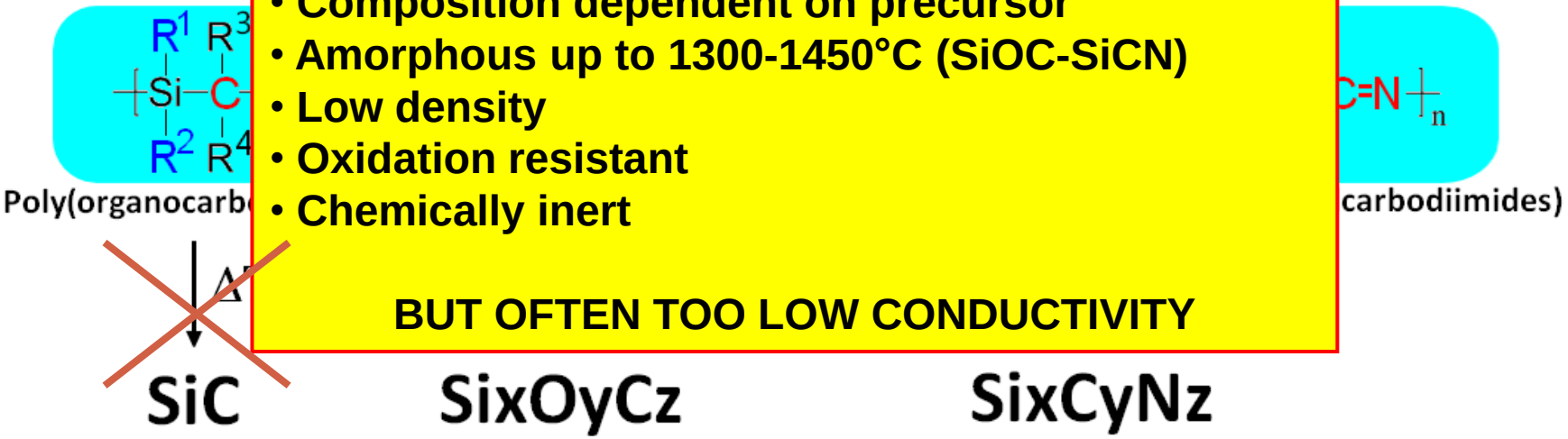
Silicon-Based Polymers: 

ADVANTAGES
- **Composition dependent on precursor**
- **Amorphous up to 1300-1450°C (SiOC-SiCN)**
- **Low density**
- **Oxidation resistant**
- **Chemically inert**

BUT OFTEN TOO LOW CONDUCTIVITY



INACTIVE VS: Li insertion

P. Colombo et al., J. Am. Ceram. Soc., **93** (2010) 1805

Our concept for improving anode materials

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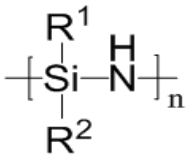
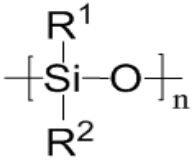
Liquid polysilazane /polysiloxane, phenyl-rich
(R^1 and/or R^2 = Ph group)

Polysilazane



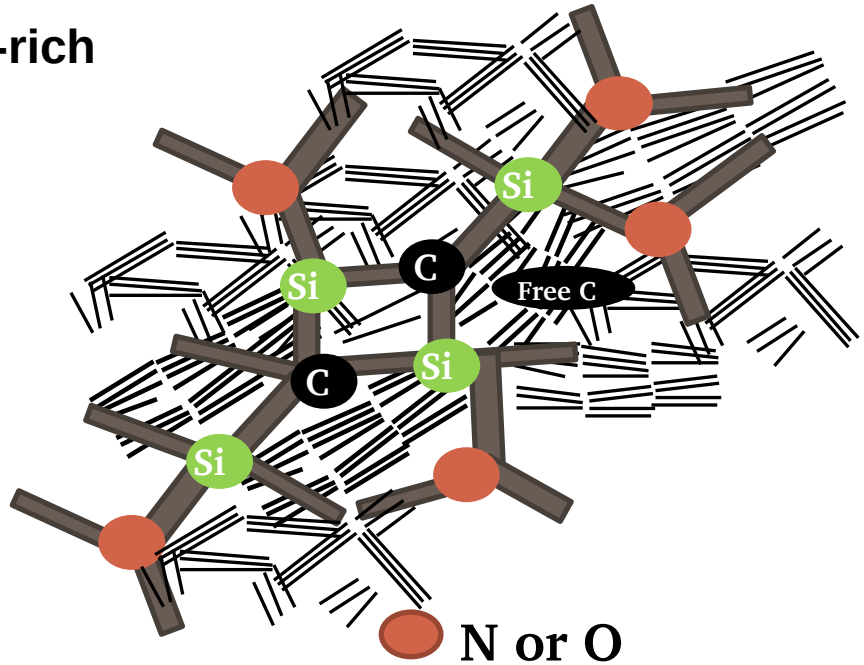
or

Polysiloxane



1000 – 1100 °C

Ar



Free carbon phase:

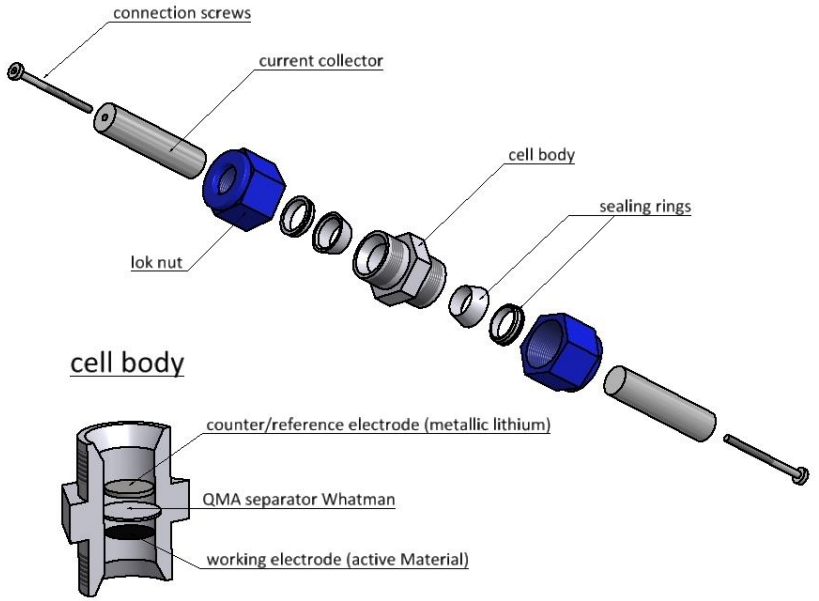
- **Increase of the electronic conductivity**
- **Increase of lithium storage capacity**

M. Graczyk-Zajac et al., J. Eur. Ceramic Soc. 30 (2010) 3235, J. Kaspar et al., Electrochim. Acta, 56 (2010) 174, L.M. Reinold et al., J. Power Sources, 236 (2013) 224, M. Graczyk-Zajac et al, Solid State Ionics 225 (2012) 522, J. Kaspar et al., Solid State Ionics 225 (2012) 527, J. Kaspar et al., J. Power Sources 224 (2013) 450, J. Kaspar et al., Electrochimica Acta 115 (2014) 665, M. Graczyk-Zajac et al., J. Power Sources, 196 (2011) 6412, M. Wilamowska et al., J. Power Sources (2013), P. Dibandjo, et al. J. Eur. Ceram. Soc. 32 (2012) 2495, G. Liu et al. Electrochim. Acta, 106 (2013) 101, V.S. Pradeep et al., Electrochim. Acta 119 (2014) 78, V.S. Pradeep et al. Solid State 262 (2014) 22, S.-H. Baek et al. J. Power Sources 253 (2014) 342

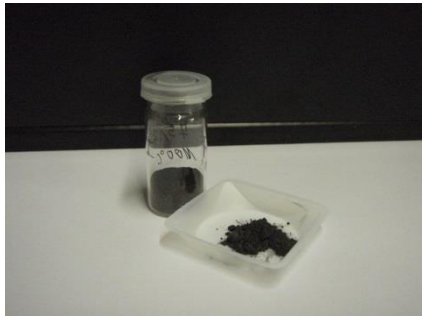
SiCN / SiOC anode materials:

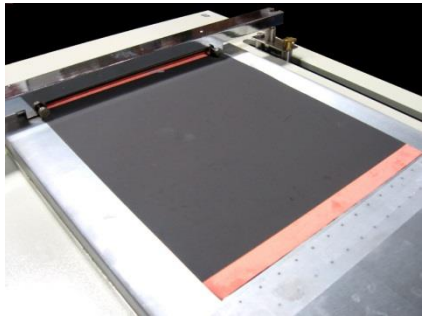
Electrode preparation

- **Grinding of pyrolyzed ceramic**
- **Sieving of powder (<40 µm)**
- **5 wt% Carbon Black Super P**
- **10 wt% PVDF (in NMP)**
- **Tape casting on copper foil**
- **Cell assembly in glovebox**



Electrode loading 4-5 mg/cm^2, 1M $LiPF_6$ in EC/DMC 1:1,
Whatmann™ glassy filter as separator,
2 electrode Swagelok® cells, C = D = 18 mA/g





Differences in storing Li-ions in SiCN / SiOC materials

Role of ceramic matrix & free carbon phase

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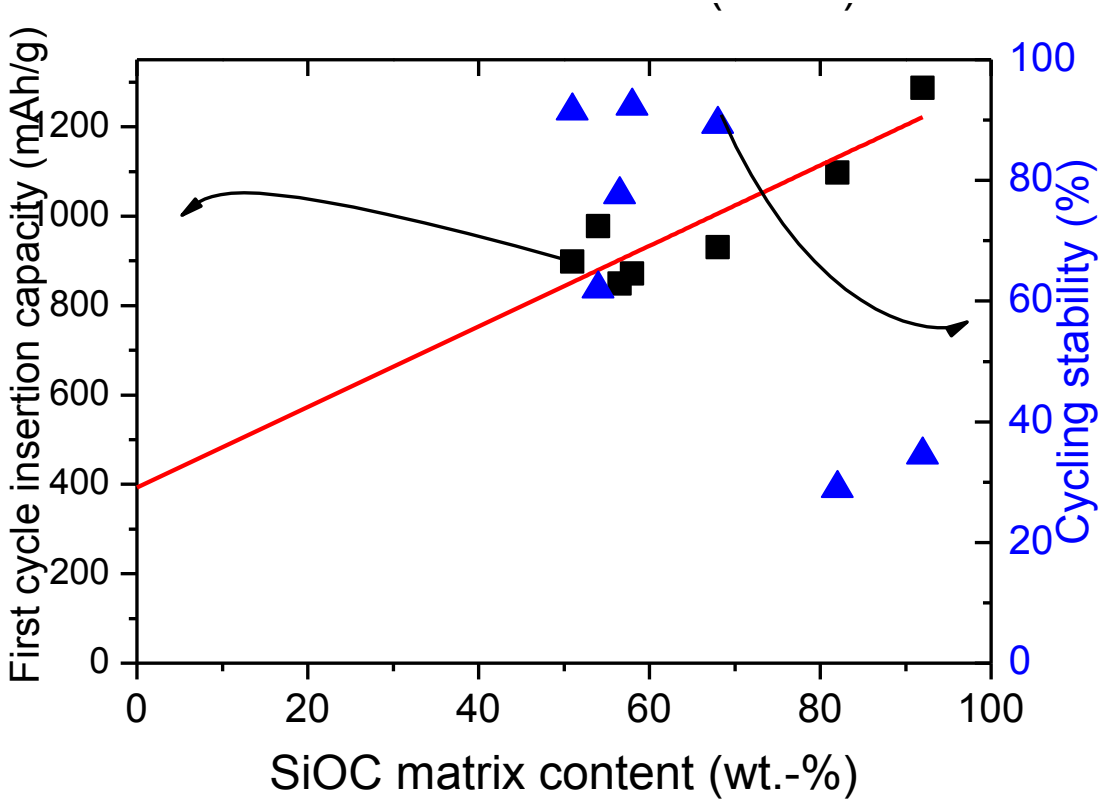
SiOC electrode materials:

Role of ceramic matrix



- **SiOC lithiation capacity: linear increase with the amount of SiOC phase up to ~ 1200 mAh/g, extrapolated to 0 % of SiOC amounts to ~ 400 mAh/g**

Cycling stability defined as the ratio of the extraction capacity after prolonged cycling (<100 cycles) to the first extraction capacity

SiCN anode materials:

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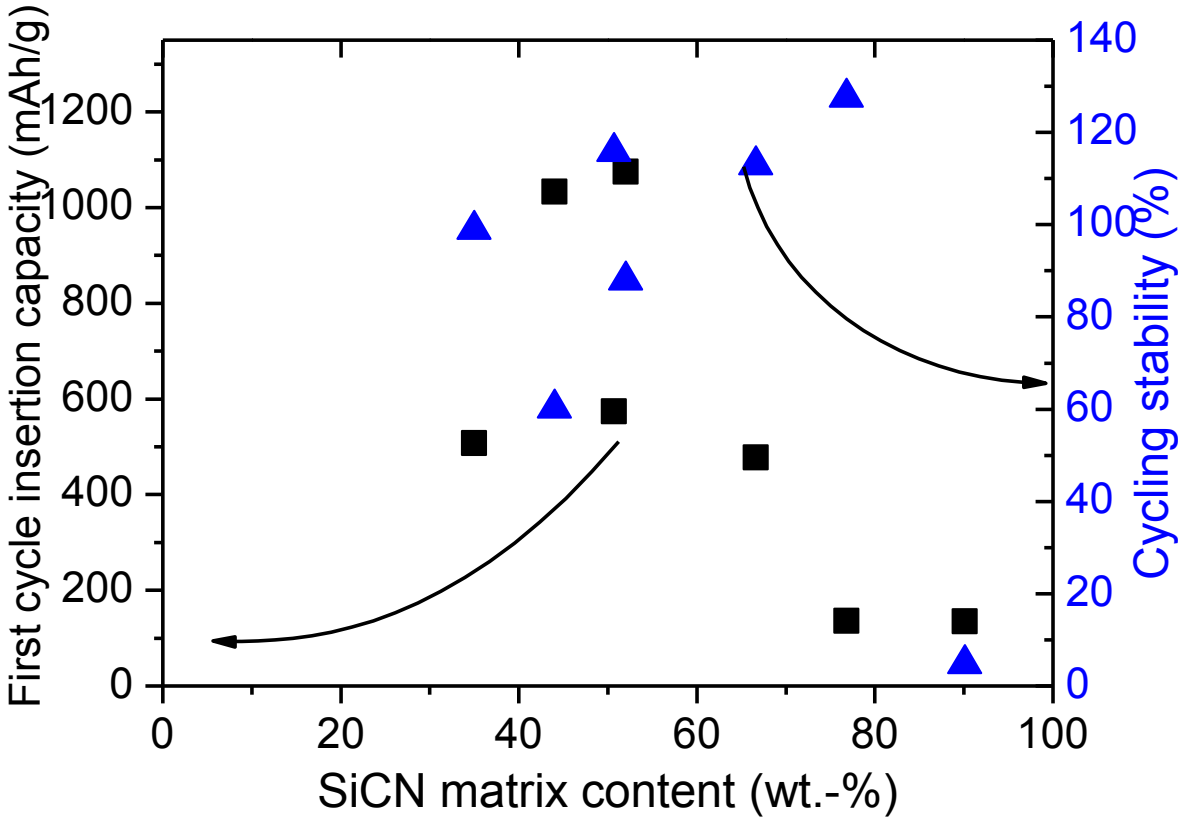
Role of ceramic matrix



- **SiCN lithiation capacity: no dependence on the SiCN matrix amount.**
- **Contrary to SiOC lithiation capacity is lower for high amount of SiCN matrix**

SiOC anode materials:

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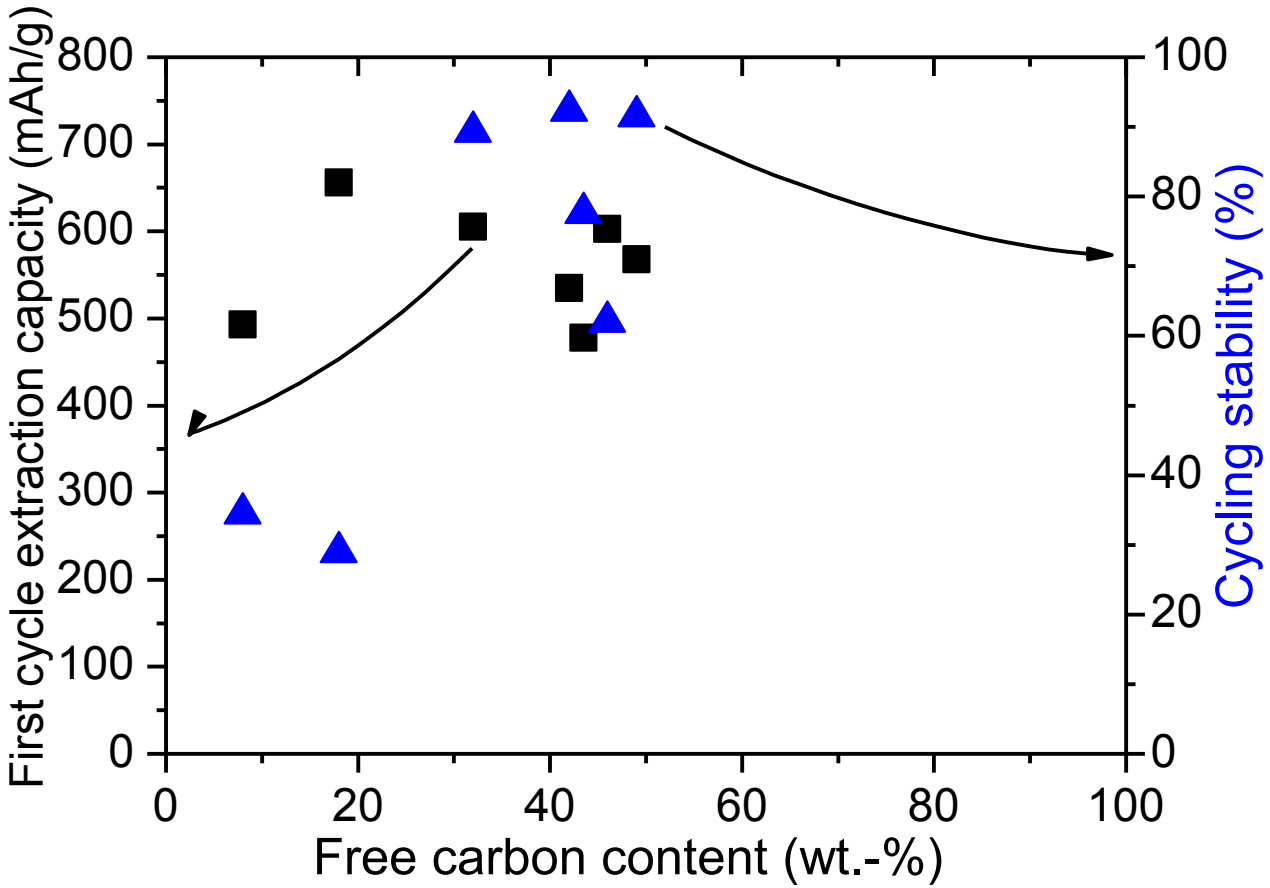
Role of free carbon phase



➢ **SiOC delithiation capacity: almost independent on the amount of free carbon**

SiCN anode materials:

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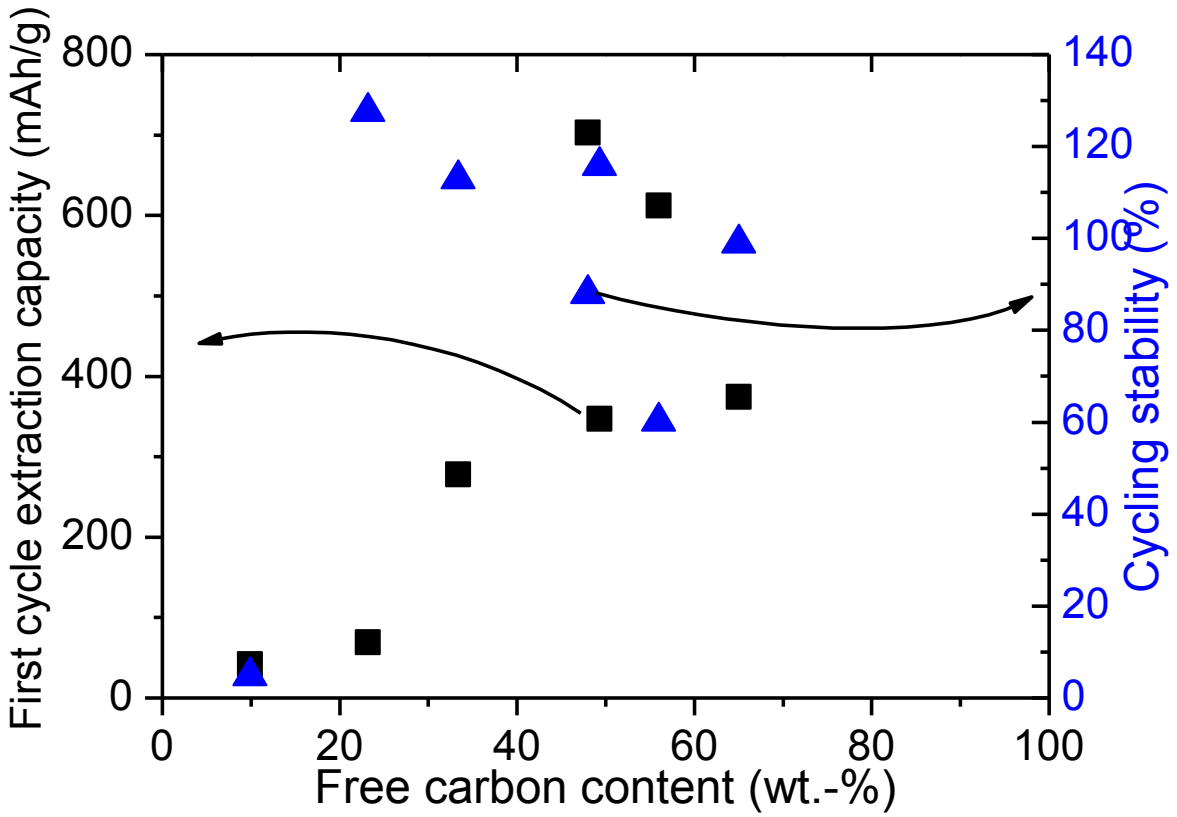
Role of free carbon phase



- **Extraction capacity: increases, to reach a threshold value at about 50% of C**
- **Cycling stability of carbon-poor SiCN low, increases with carbon amount**

What more….?

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- Si – N bond more covalent than Si – O: Li stronger attracted by O in the SiOC network due to the ionic character of Si-O bonds
- Electronegativity of oxygen and nitrogen is 3.5 and 3.1, respectively
- DFT modelling (SiOC): Li insertion into amorphous silica (a-SiO_2) and SiOC containing exclusively Si-O and Si-C bonds energetically unfavorable [2]
- Solid state NMR on SiCN: free carbon phase is a major lithium storing phase [2]

1. P. Kroll, MRS Online Proceedings Library, 1313 (2011) 1-6
2. S.-H. Baek, L.M. Reinold, M. Graczyk-Zajac, R. Riedel, B. Büchner, H.-J. Grafe J. Power Sources **253** (2014) 342

Conclusions

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- **SiOC matrix:** ceramic phase attracts Li leading to high first capacities at low carbon contents. But for carbon-poor SiOC lithium irreversibly captured => low electrochemical stability
- **SiCN matrix:** ceramic network less attractive for Li due to covalent character of Si-N bonds, insertion capacity is low for low free carbon amounts
- **Carbon-rich SiOC/SiCN:** composite materials, the free carbon phase leads to high cycling stability and both to irreversible and reversible capacities, the ceramic matrix is indispensable to insure the stability of the free carbon phase within the prolonged cycling

Conclusions

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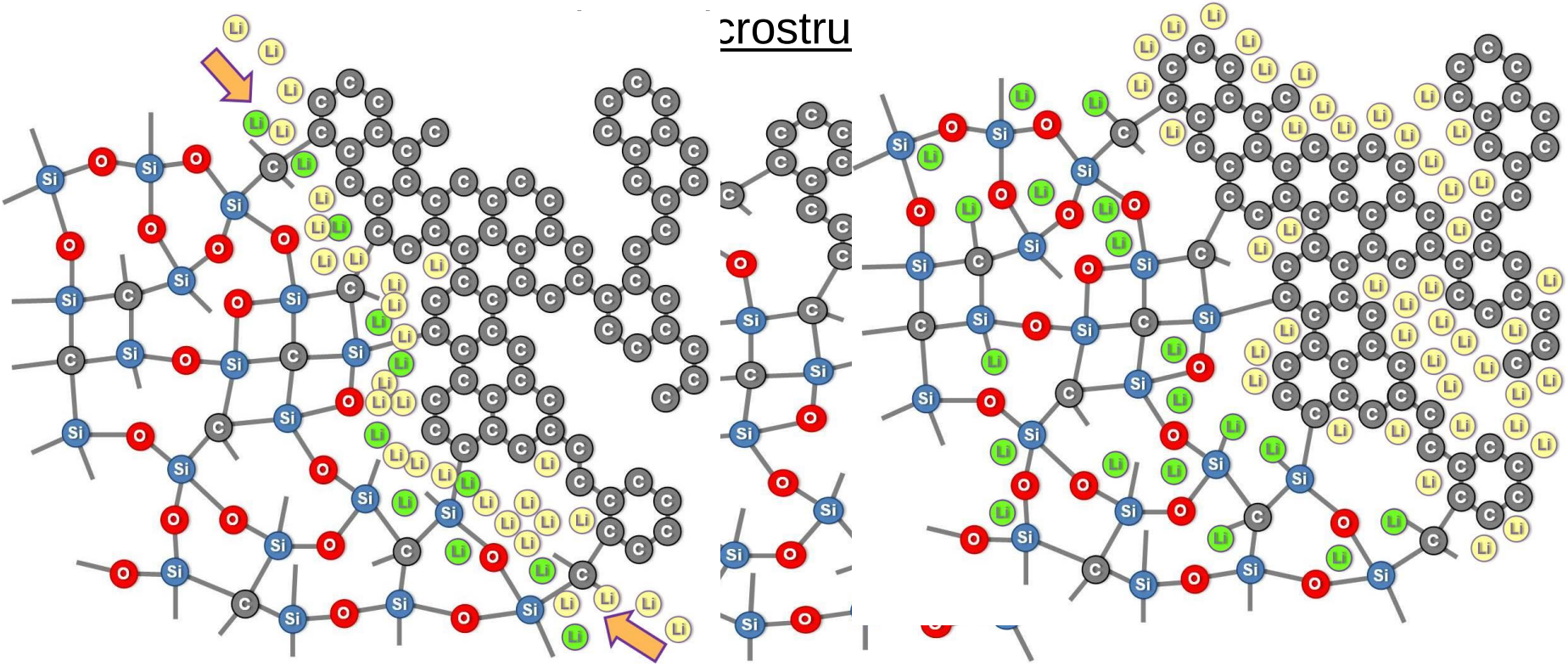
Li-ion insertion, diffusion

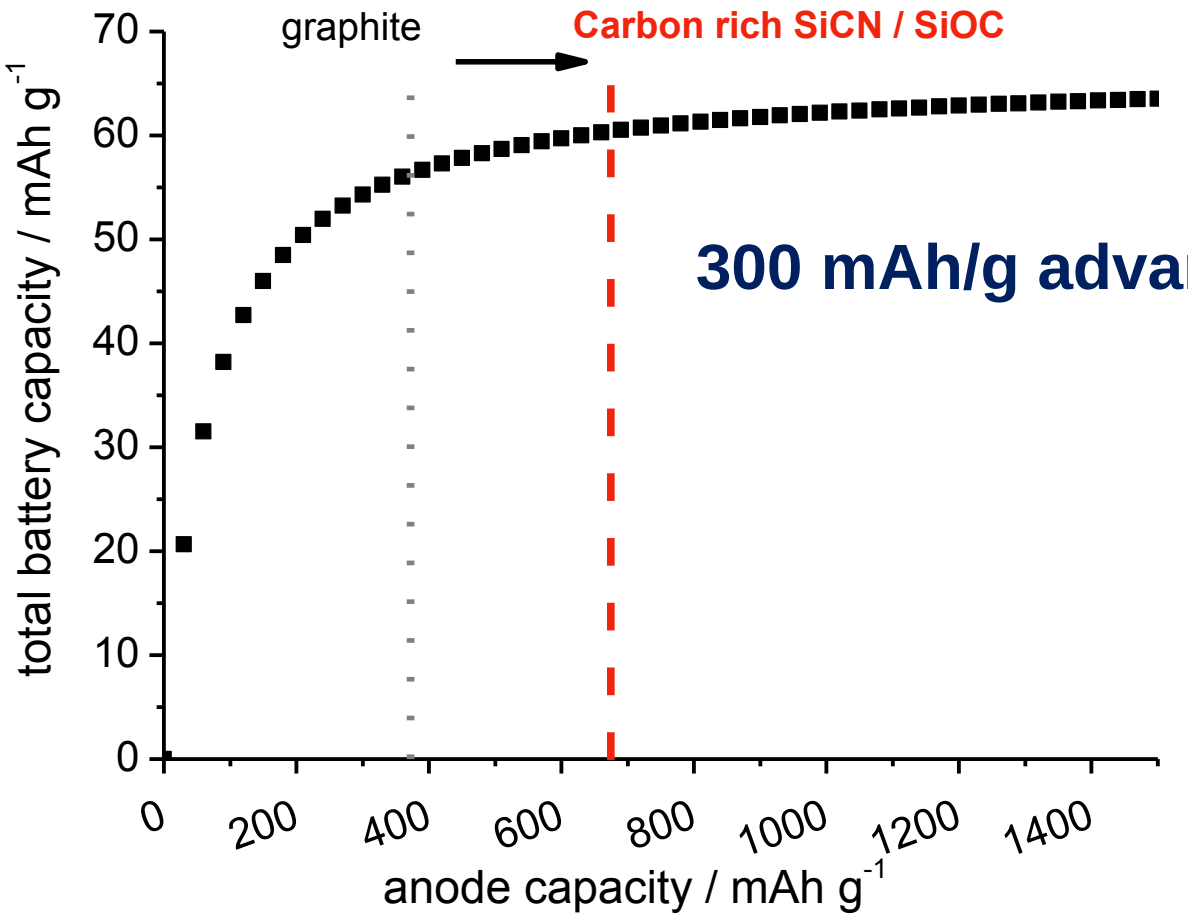
crostru

Li-ion storage



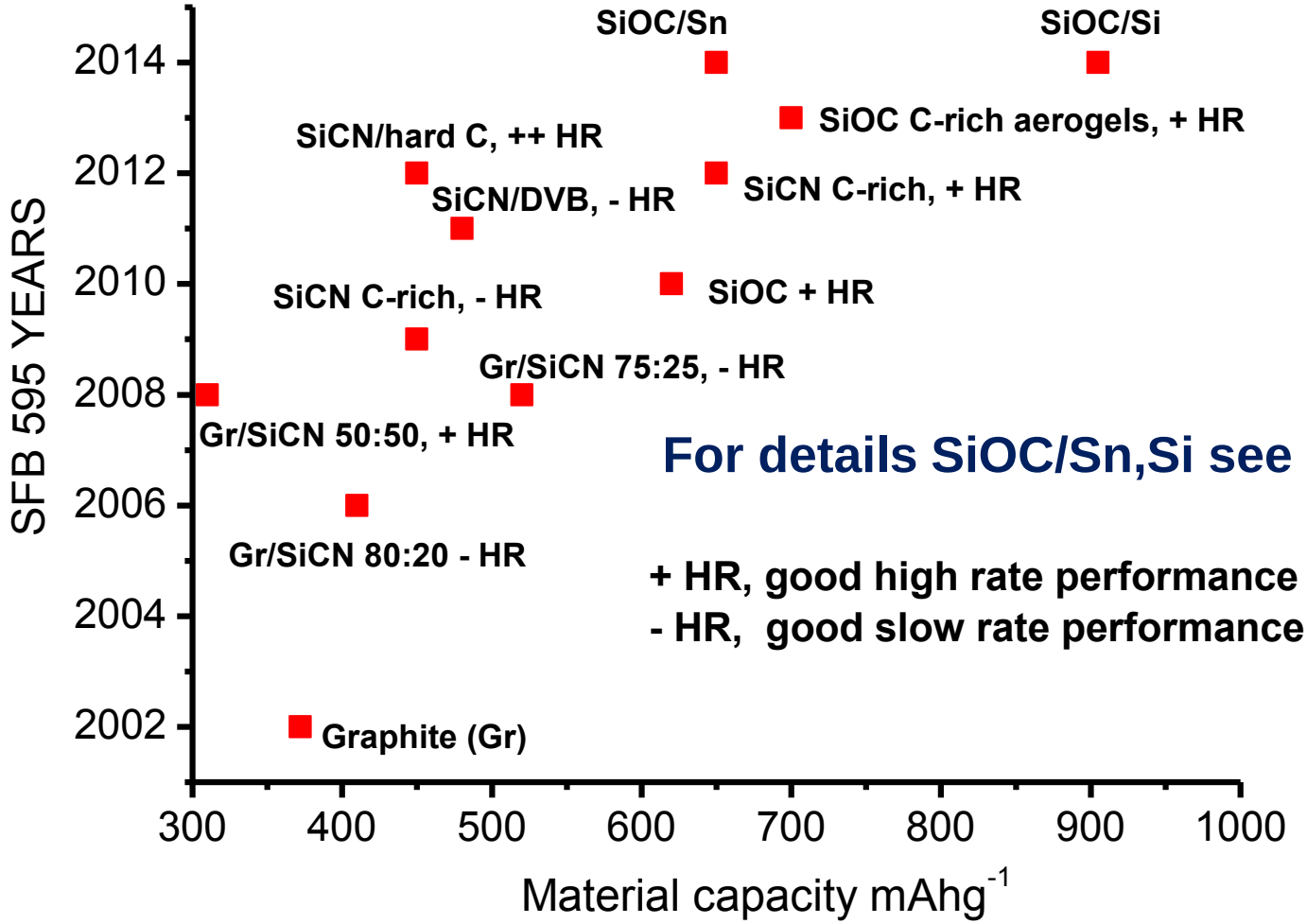
J. Kaspar, for detailed discussion see poster P14: A4

Conclusions



300 mAh/g advance over graphite!

Conclusions



For details SiOC/Sn,Si see poster P14:A4

+ HR, good high rate performance
- HR, good slow rate performance

Thanks to

TECHNISCHE UNIVERSITÄT DARMSTADT

R. Riedel, G.D. Soraru, H. Ehrenberg

C. Fasel, G. Völzke

Jan Kaspar, Guanwei Liu, Mirko Reinold, Pradeep Vallachira, Monika Wilamowska

S.-H. Baek, H.-J. Grafe

SFB 595 „Gender-equality“ financial support to balance career and family life

You for your attention!

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