Speichermaterialien für Li-Ionen-Batterien: Composite-Anoden

FVEE-Workshop
Elektrochemische Energiespeicher und Elektromobilität

19.1.2010

H. Wolf (hannes.wolf@uni-bayreuth.de)

Prof. Dr. M. Willert-Porada

Die Speicherung von elektrischer Energie in Lithiumionenbatterien ist ein Thema, was im Automobilbereich im Hinblick auf Hybrid- und Elektrofahrzeuge zunehmend an Bedeutung gewinnt. Materialseitig besteht hier aber noch großer Entwicklungsbedarf hinsichtlich einer Erhöhung von spezifischer Kapazität der Werkstoffe und Batteriesysteme, denn gerade Gewicht und zur Verfügung stehender Einbauraum sind im Fahrzeug von konstruktiver Seite aus begrenzt. Zudem muss die Sicherheit sowie die Schnellladefähigkeit der Batterien gewährleistet sein.

Die zurzeit eingesetzten Li-Ionenbatterien verfügen über Graphitanoden, welche nur eine begrenzte spezifische Kapazität aufweisen. Auf dem Papier signifikat überlegene Systeme wie beispielsweise Lithium-Schwefel Batterien oder gar Lithium-Luft Batterien, sind technisch noch lange nicht ausgereift und werden vermutlich frühestens in einigen Jahrzehnten für kommerzielle Anwendungen zur Verfügung stehen, so dass zur Überbrückung dieser Zeitspanne eine Weiterentwicklung der bestehenden Li-Ionenbatterien hinsichtlich höherer spezifischer Kapazität notwenig ist.

Neben dem Graphit bieten sich auch alternative Materialien, wie Zinn, Aluminium oder Silizium für den anodenseitigen Einsatz an, welche über hohe theoretische Kapazitäten verfügen. Die Einlagerung von großen Mengen an Lithium führt dort jedoch zu großen Volumenänderungen, die rasch zur Zerstörung der Materialien führen kann, zudem ist oft die niedrige elektrische Leitfähigkeit ein limitierender Faktor, gerade im Hinblick auf Schnelladefähigkeit.

Für eine Steigerung der spezifischen Kapazität von Lithium-Ionenbatterien gegenüber Graphitanoden bieten sich daher Composite-Materialien an, welche neben dem Kohlenstoff für gute elektrische Leitfähigkeit auch einen Anteil an nanostrukturierten Materialien mit überlegener spezifischer Kapazität enthalten.

Dieser Vortrag gibt zunächst einen kurzen Überblick über verschiedene Zinn- und Siliziumkompositwerkstoffe, welche in der Literatur in den vergangenen Jahren beschrieben wurden, und stellt dann einen an der Universität Bayreuth entwickelten Kohlenstofffaser-Silizium-Nanocomposite-Werkstoff etwas detaillierter vor.

Outline

1 Why Composite Anodes?

2 Requirements for composite anodes

3 Sn-composite anodes

4 Si-composite anodes

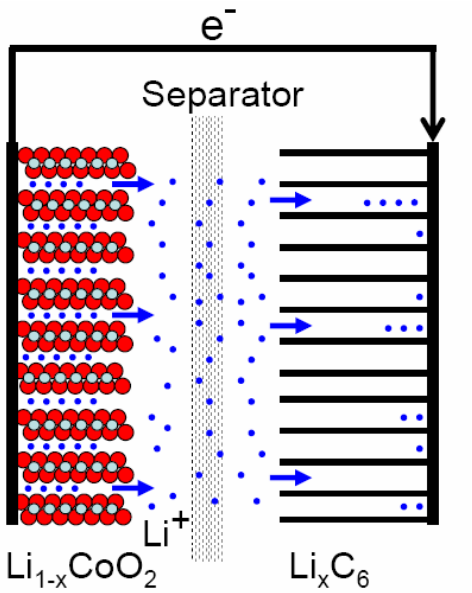
5 Multifunctional Carbon-Silicon-Nanocomposite

6 Outlook

Why Composite Anodes?

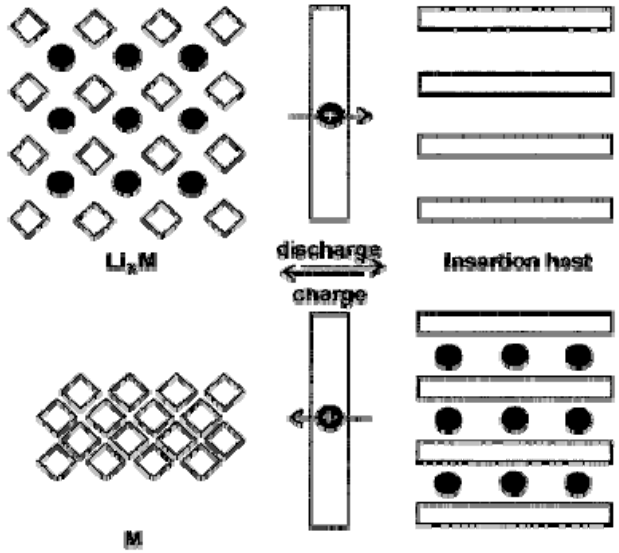
State-of-the Art: Graphite, Li is intercalated

+ Good cycling stability
+ High electric conductivity
+ Only slight volume changes
- Limited specific capacity



Metals forming binary electrochemically active alloys with Li

- Poor cycling stability
- Often limited electric conductivity
- Significant volume changes
+ High theoretical specific capacity



M. Winter, J.O. Besenhard, M.E. Spahr, P. Novak, Advanced Materials 10 (1998), 725-763.

Outline

1 Why Composite Anodes?

2 Requirements for composite anodes

3 Sn-composite anodes

4 Si-composite anodes

5 Multifunctional Carbon-Silicon-Nanocomposite

6 Outlook

Requirements for composite anode materials

Nanostructured high capacity materials combined with highly conductive support

=> short diffusion paths, reduced mechanical stress during cycling

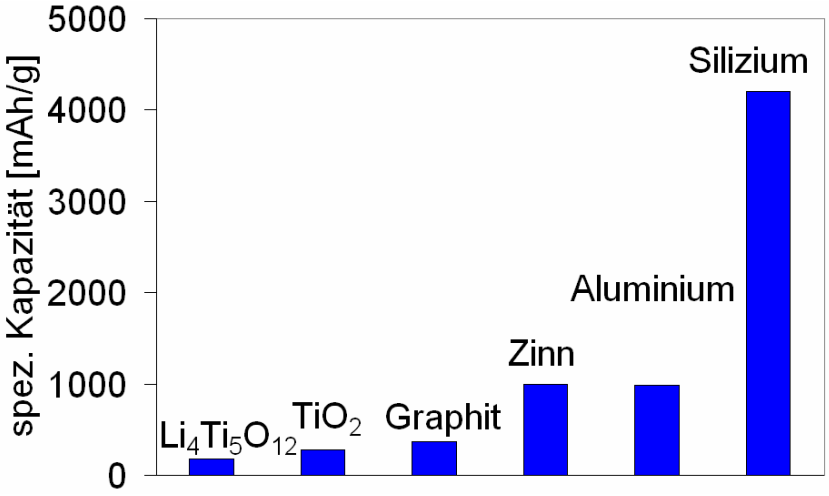
Large Li-ion diffusivity and high electrical conductivity

=> Higher charge / discharge current

Chemical stability against electrolyte

=> Safety

Flat voltage plateau



Outline

1 Why Composite Anodes?

2 Requirements for composite anodes

3 Sn-composite anodes

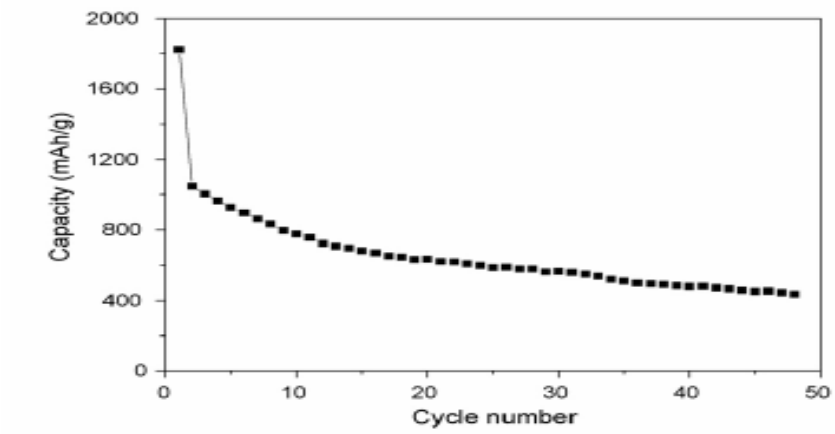
4 Si-composite anodes

5 Multifunctional Carbon-Silicon-Nanocomposite

6 Outlook

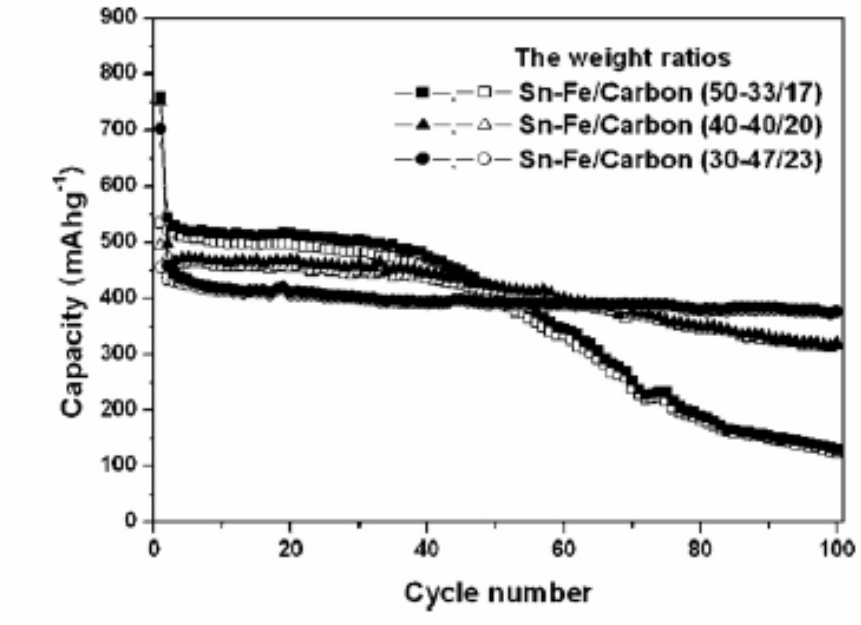
Sn-composite anodes

SnO_2 nanotubes mixed with carbon

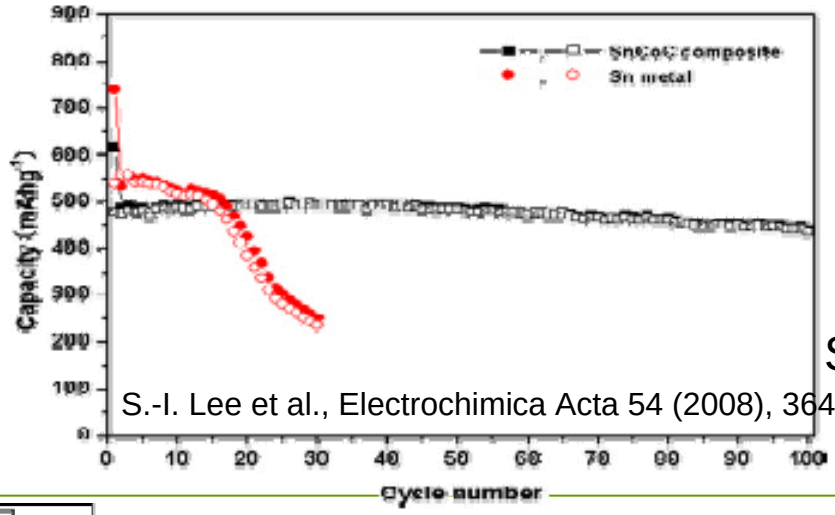


N. Du, H. Zhang et al., Materials Research Bulletin 44 (2009), 211–215.

Sn-Fe/C nanocomposite



S. Yoon et al., Electrochimica Acta 54 (2009), 2699–2705.



S.-I. Lee et al., Electrochimica Acta 54 (2008), 364–369.

SnCoC composite vs. Sn particles

Sony: Nexelion™

Commercial battery with Sn-composite anode

- Anode: 50 wt.% graphite, 25wt.% Co, 25wt.% amorphous tin [1]
- Kathode: mixture of $LiCoO_2$ + $Li(Co_yNi_{1.7x}Mn_x)O_2$ [1]
- Reversible specific capacity (anode) ~500 mAh/g [2]
- + 30% volumetric energy density, + 10% specific energy density (compared to a conventional graphite / $LiCoO_2$ cell)

Image: Sony

[1] J. Wolfenstine, J.L. Allen, J. Read, D. Foster, Chemistry and Structure of Sony's Nexelion Li-ion Electrode Materials, Progress Report Feb-Apr 2006, Army research lab Adelphi MD sensors and electron devices directorate, A783974.

[2] G. Derrien, J. Hassoun, S. Panero, B. Scrosati, Adv. Mater. 19 (2007), 2336–2340.

Outline

1 Why Composite Anodes?

2 Requirements for composite anodes

3 Sn-composite anodes

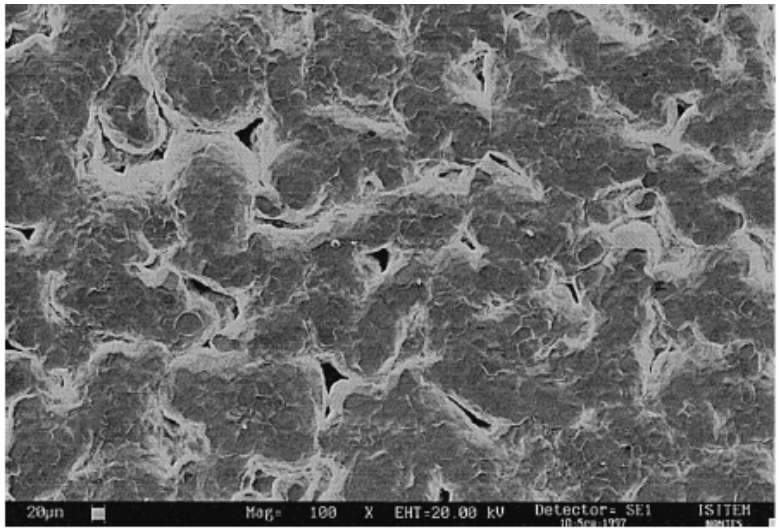
4 Si-composite anodes

5 Multifunctional Carbon-Silicon-Nanocomposite

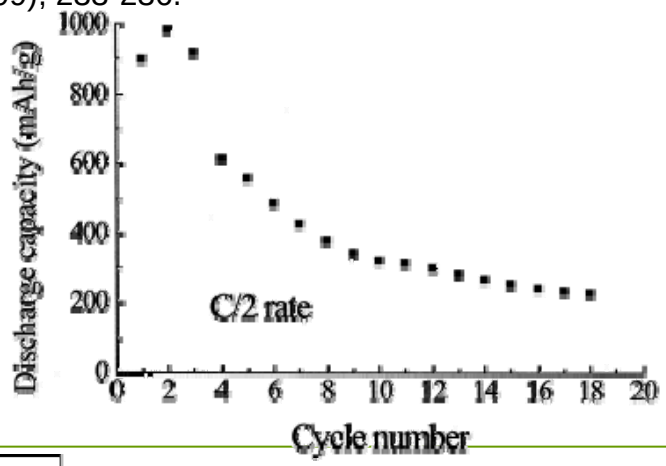
6 Outlook

Si-composite anodes

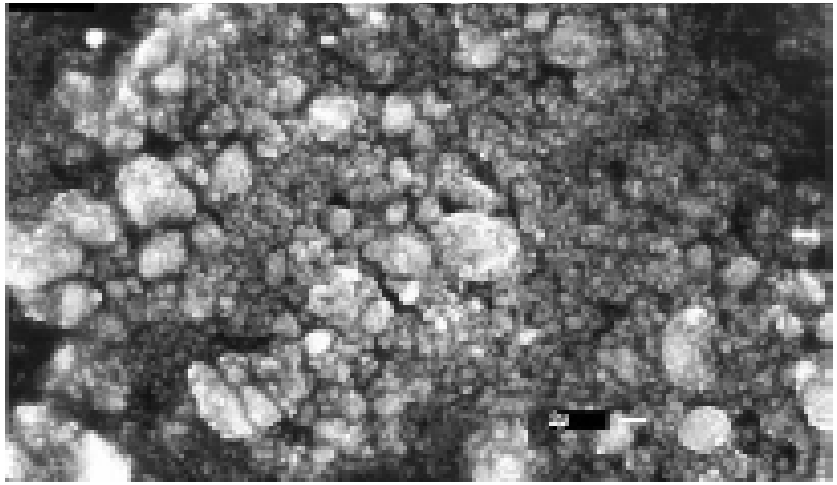
1,2 µm Si layer on porous Ni



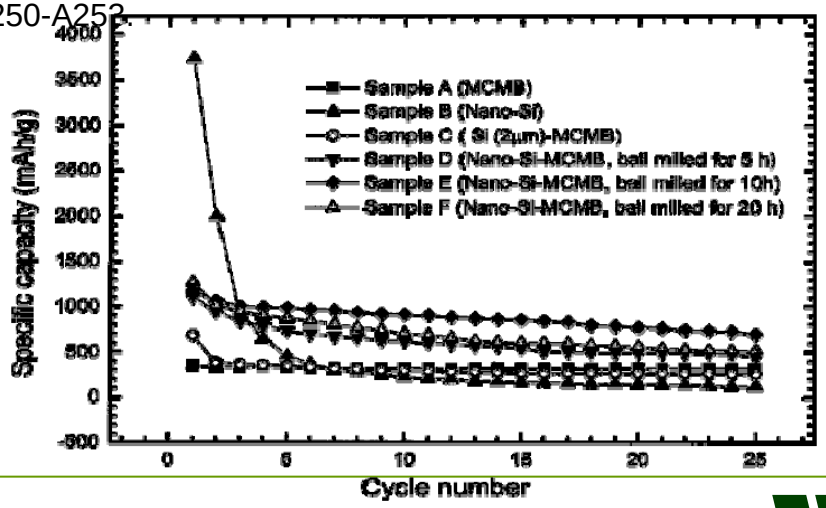
S. Bourderau, T. Brousse, D. Schleich, J. Power Sources 82 (1999), 233-236.



Nano-silicon, ballmilling with graphite

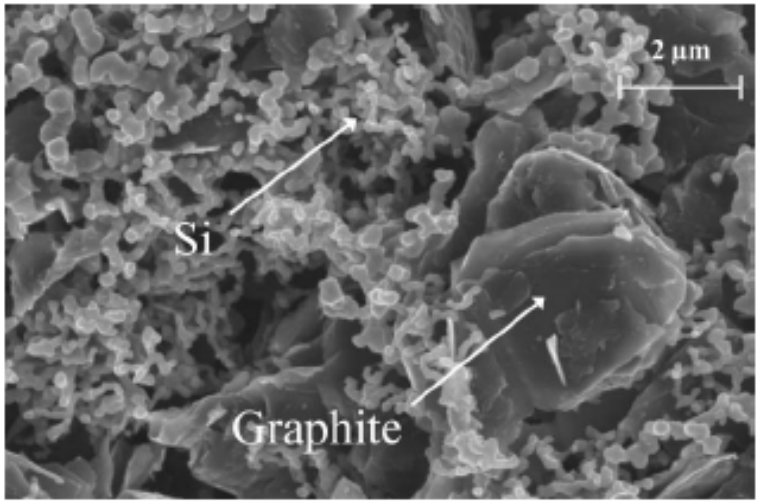


G.X. Wang, J. Yao, H.K. Liu, Electrochem. Solid State Lett. 7 (2004), A250-A253.

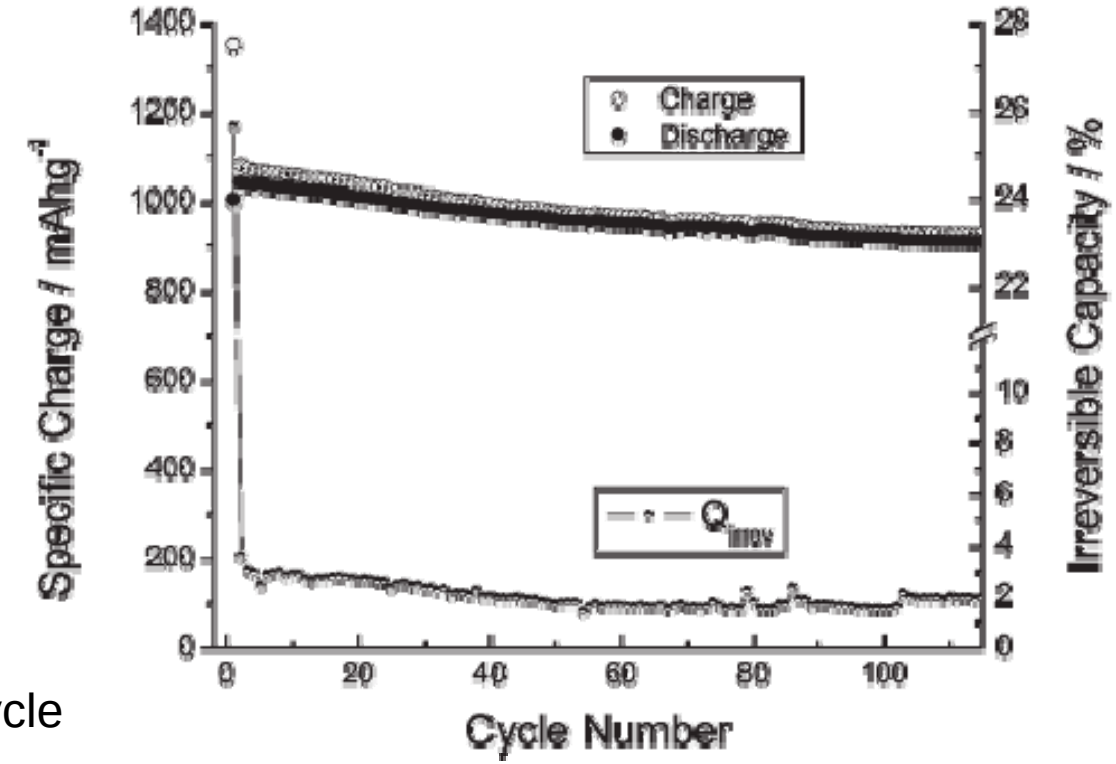


Si-composite anodes

Nanostructured silicon by SiH_4 pyrolysis, mixed with graphite



M. Holzapfel, H. Buqa, W. Scheifele, P. Novak, F.-M. Petrat, Chemical Communications (2005), 1566-1568.

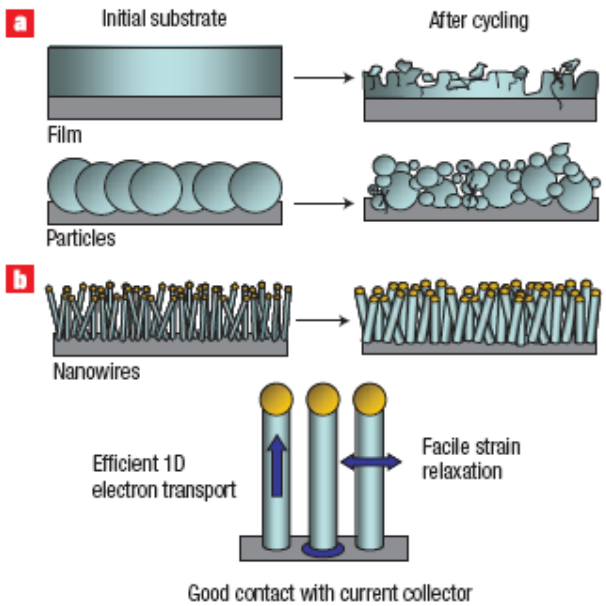


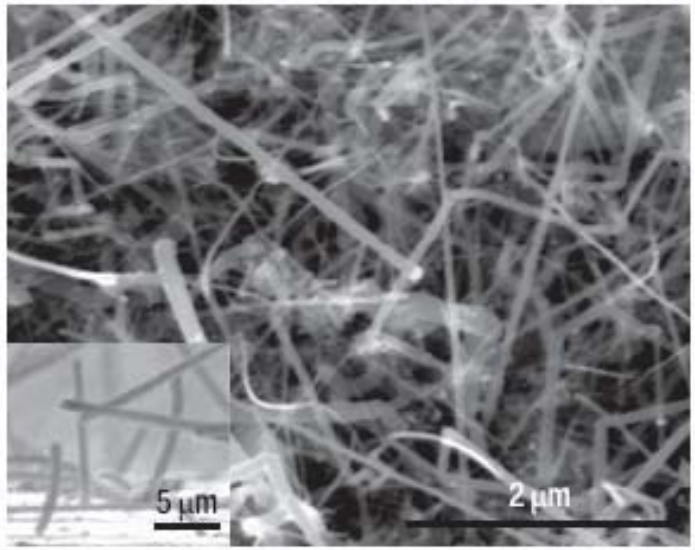
~28% irreversible capacity in first cycle

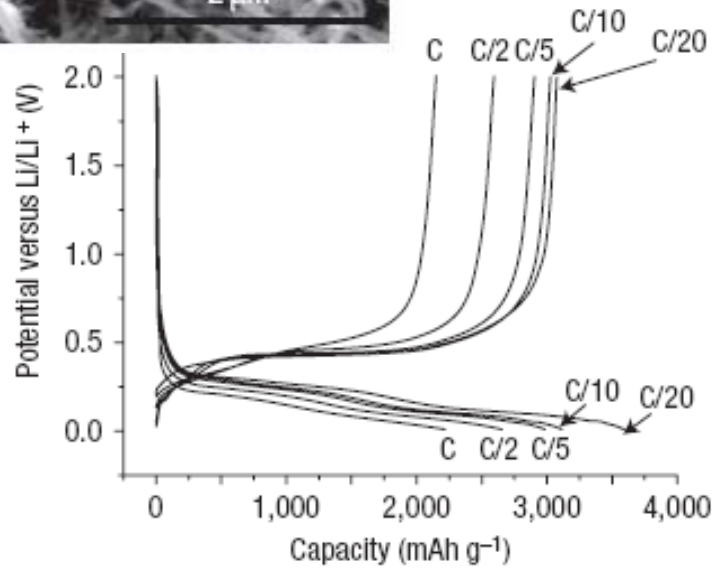
Constant capacity fading

Limited charge/discharge current (cc-cv C/5-C/80 !)

Si nanowires on metallic support







1-dimensional expansion is beneficial for reducing mechanical stress during cycling

C.K. Chan, R.A. Huggins et al., Nature Nanotechnology 3 (2008), 31-35.

C.K. Chan, R. Ruffo, S.S. Hong, Y. Cui, J. Power Sources 189 (2009), 1132–1140.

Outline

1 Why Composite Anodes?

2 Requirements for composite anodes

3 Sn-composite anodes

4 Si-composite anodes

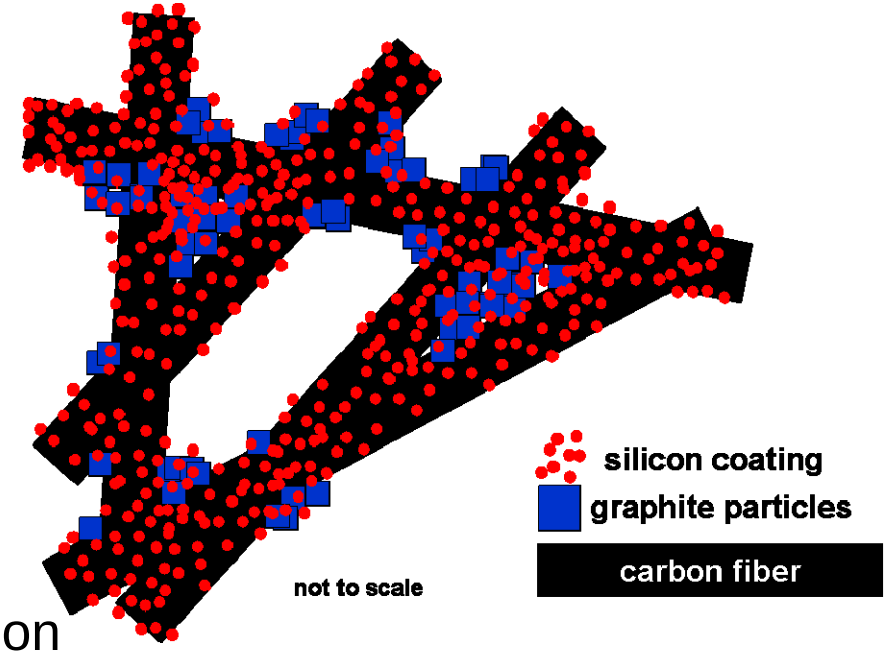
5 Multifunctional Carbon-Silicon-Nanocomposite

6 Outlook

Multifunctional Carbon-Silicon-Nanocomposite

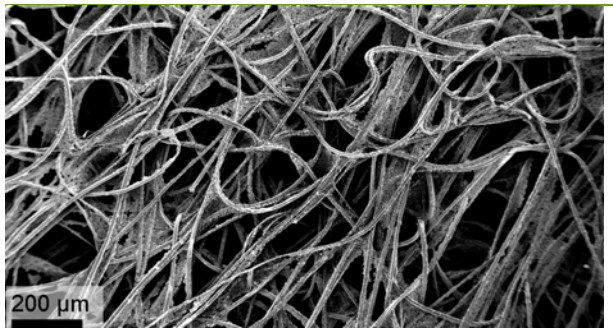
Deposition of nano-silicon on a carbon-fiber substrate by plasma enhanced chemical vapor deposition

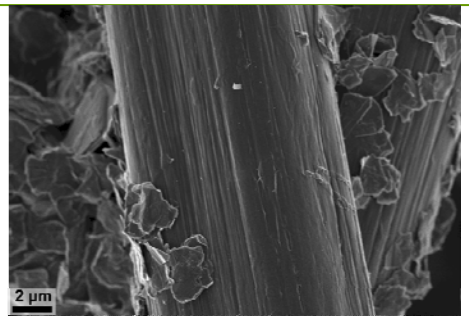
H. Wolf, Z. Pajkic, T. Gerdes, M. Willert-Porada, Carbon-Fiber-Silicon-Nanocomposites for Lithium-Ion Battery Anodes by Microwave Plasma Chemical Vapor Deposition, Journal of Power Sources 190 (2009), 157-161.



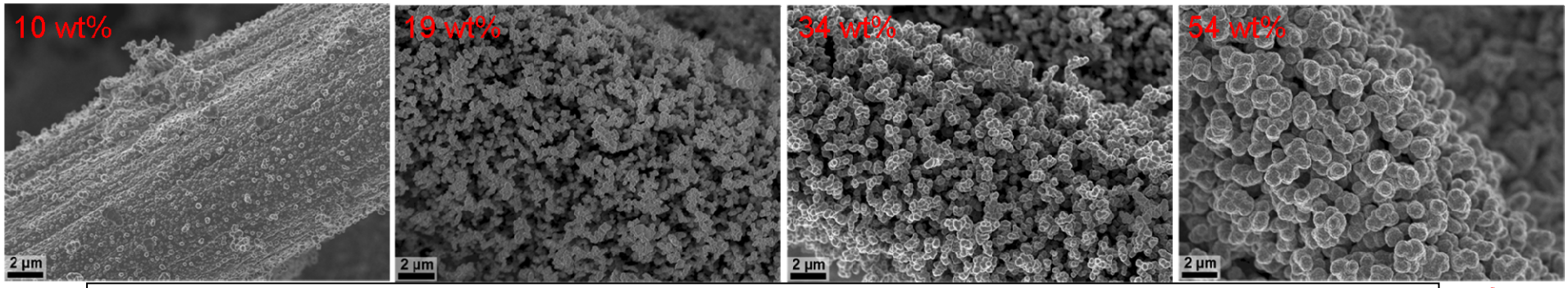
- Fiber substrate: large area for Si deposition
- Percolating network ➔ electrical conductivity, mechanical stability
- Insertion of Li in both Si and C
- Additional carbon coating for enhanced conductivity
- Anode material free of polymeric binder

Multifunctional Carbon-Silicon-Nanocomposite

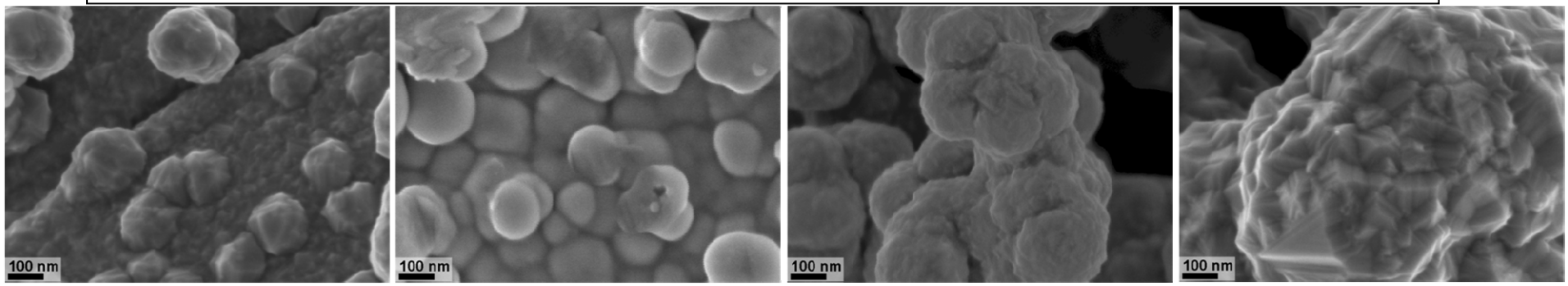




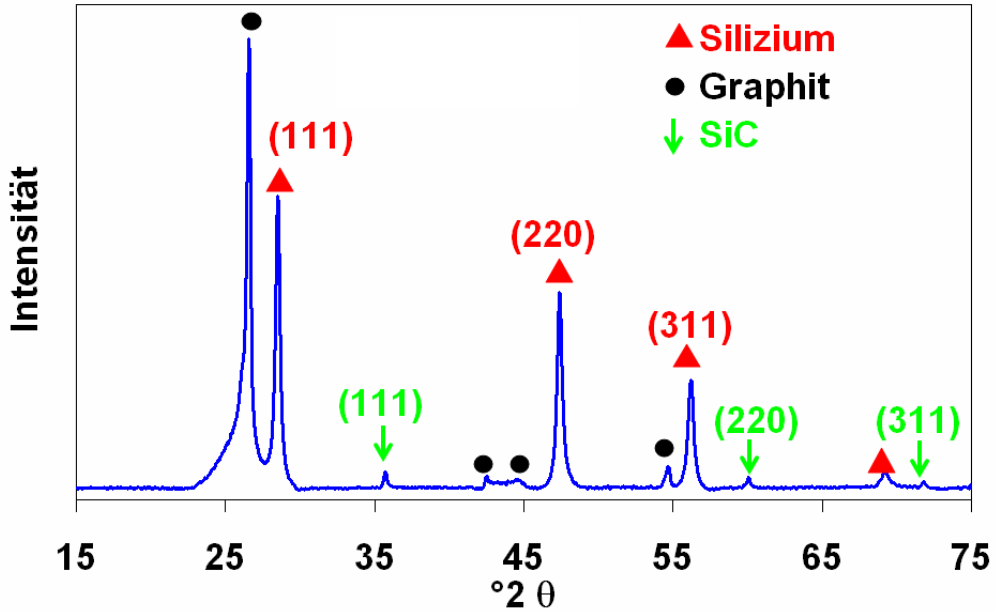
Uncoated substrate: Commercial gas diffusion layer



Increasing coating time, Silicon loading, coarsening of Si-particles



Multifunctional Carbon-Silicon-Nanocomposite

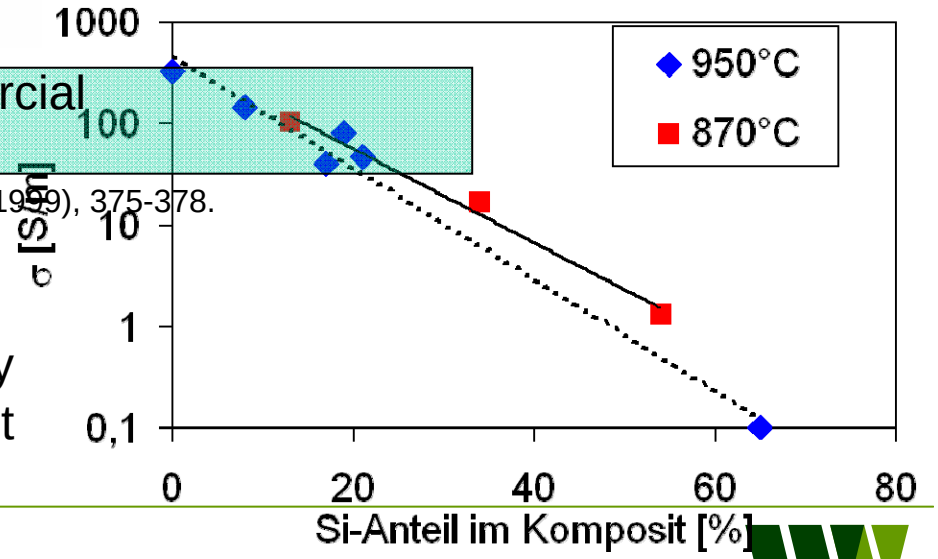


XRD: ~ 20 wt.% Si after 60 s PE-CVD

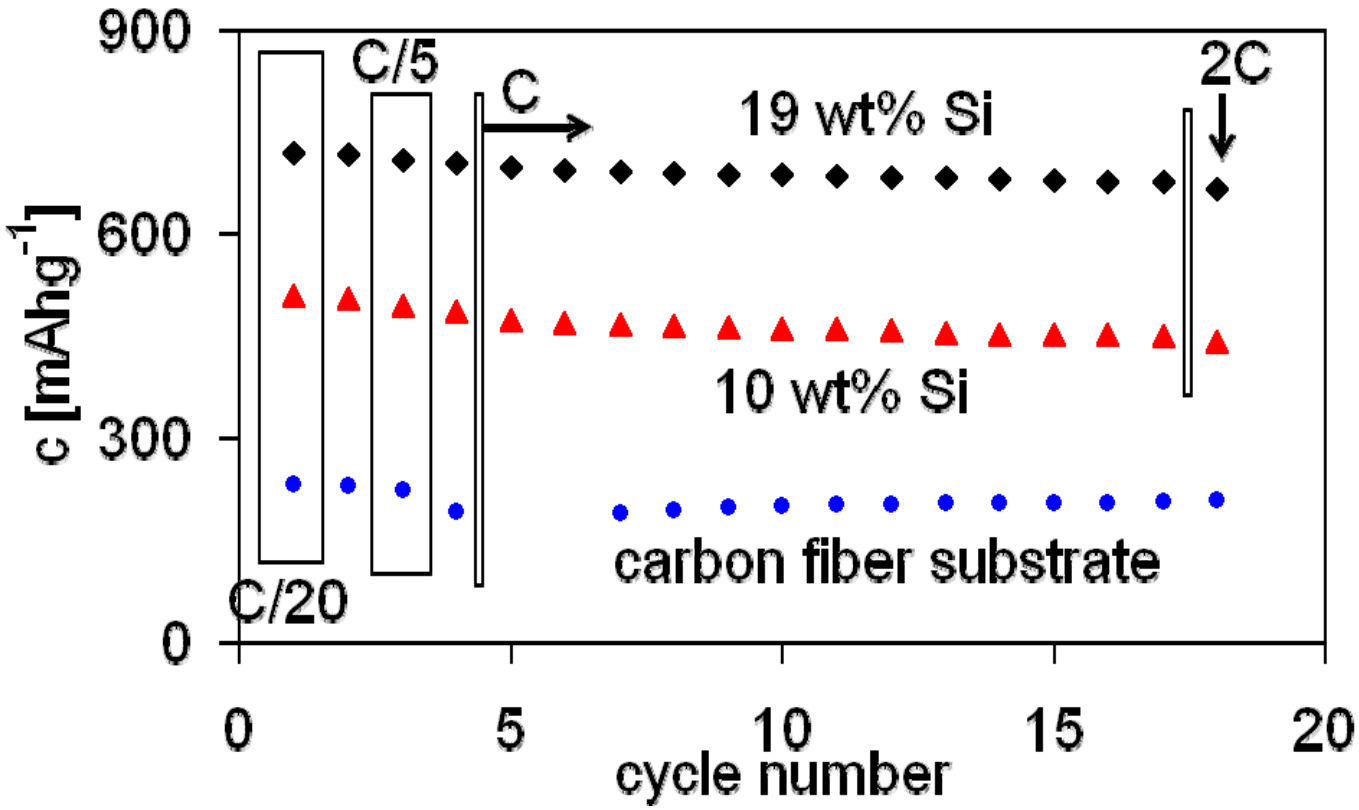
conductivity of commercial carbon anodes

M. Nishizawa et al., Electrochemistry Communications 1 (1999), 375-378.

Specific electrical conductivity depending on Si content

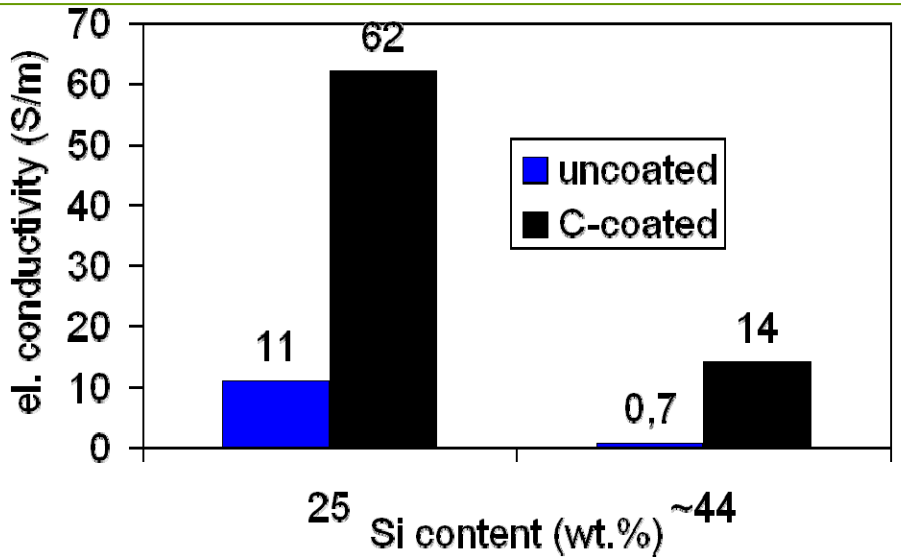


Cycling of C-Si-Nanocomposite anodes



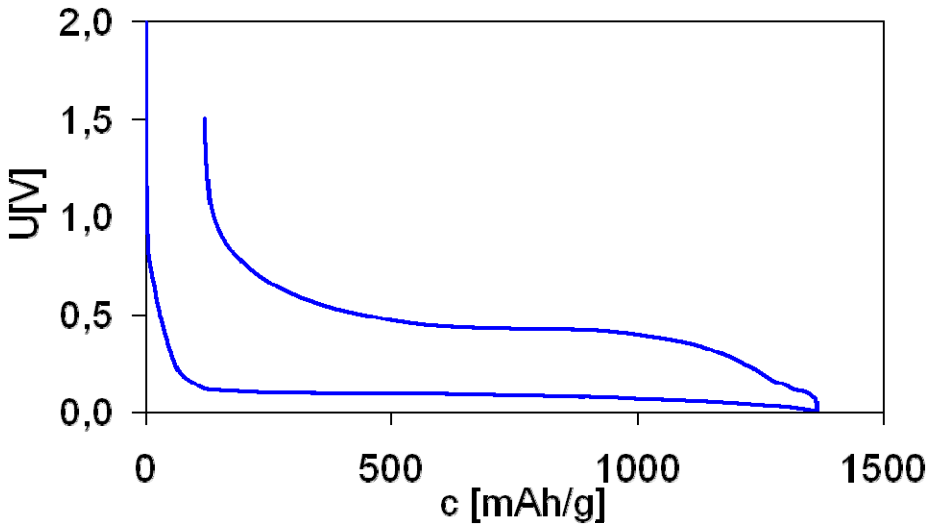
reversible specific capacity for different Si concentrations and increasing charge/discharge current

Effect of pyC coating on C-Si-Nanocomposites

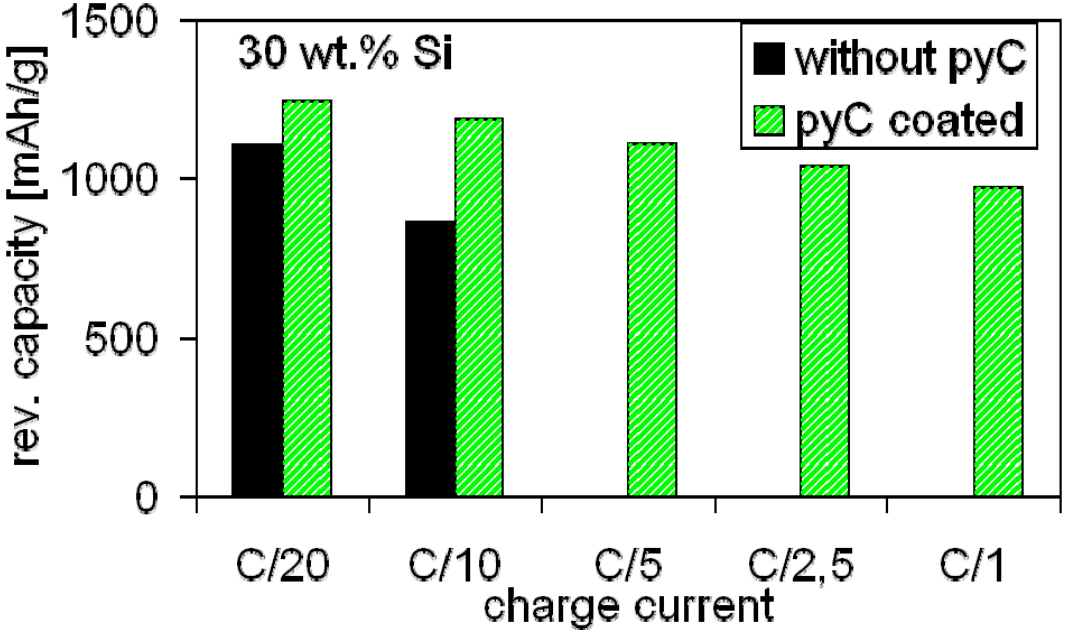


Significant increase of electrical conductivity after additional coating with pyrolytic carbon (pyC).

Formation of SEI in first cycle
C/20, ~30 wt.% Si, coated with pyC
c_{irr} only 8.8%



Effect of pyC coating on C-Si-Nanocomposites



~1000 mAh/g reversible specific capacity at high charge / discharge current

Outline

1 Why Composite Anodes?

2 Requirements for composite anodes

3 Sn-composite anodes

4 Si-composite anodes

5 Multifunctional Carbon-Silicon-Nanocomposite

6 Outlook

Outlook

- Nanostructured composite anodes have the potential to replace graphite anodes in the future, with the first systems already being commercialized (e.g. Nexelion).

- Especially for applications in automotive industry, cells with composite anodes are interesting due to their increased volumetric and specific energy density, as both volume and weight are important factors in construction.

- Still, extensive research and testing has yet to be done, in order to get information about lifetimes matching the demands of automotive industry (i.e. ~10 years)

Thank you for your attention!