Design and characterization of silicon-based composites in lithium-ion batteries: An overview of material structures and corresponding wet-chemical routes

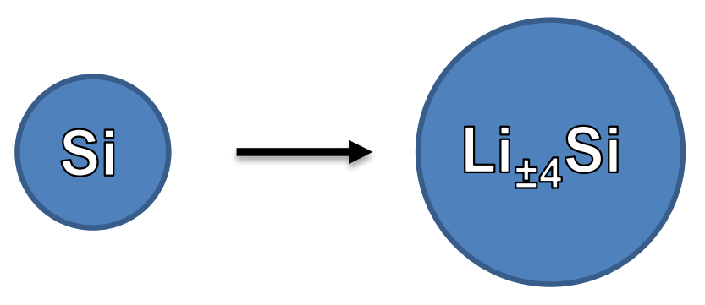
G. Bonneux, A. Hardy, F. U. Renner

Hasselt University, Institute for Materials Research (IMO), and IMEC vzw, division IMOMEC, Martelarenlaan 42, 3500 Hasselt

Introduction:

As the market share of electric vehicles (EVs) is expected to rise immensely over the next decades, the demand for improved energy storage technologies is currently at an all-time high. Silicon is regarded as a promising anode material due to its extremely high capacity and high energy density, but suffers from drastic volume changes during cycling. These cyclic volume changes lead to structural degradation of the electrode, including fracturing and loss of contact with the current collector. Importantly, the solid electrolyte interphase (SEI) formed at the surface of the Si particles has to be reformed after each cycle, which ultimately leads to capacity fading and poor cycling performance. A proposed strategy to minimize these issues is to incorporate Si nanostructures inside a (porous) composite matrix, which can reversibly accommodate the volume expansion during lithiation while also stabilizing the SEI layer. Typically, this matrix is carbon-based (amorphous, hard carbon and/or graphitic) due to its excellent conductive properties and mechanical rigidity. A number of designs such as nanoparticles, core-shell/yolk-shell structures, and more advanced architectures are reviewed and discussed, with a focus on (easily upscalable) wet-chemical routes. Furthermore, some attention is given to the chemical and morphological characterization of these structures and their interfaces, as these are critical to the stability and cycle life of the anode coating.

Composite design:



Silicon vs. Graphite

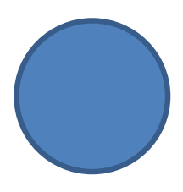
- Capacity: ~3600 mAh/g
- 4 Li for each Si
- Alloying type
- Very high volume changes (~400%)

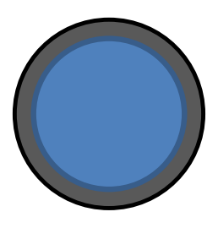
- Capacity: 372 mAh/g
- 1 Li for each 6 C
- Intercalation type
- Low volume changes (~10%)

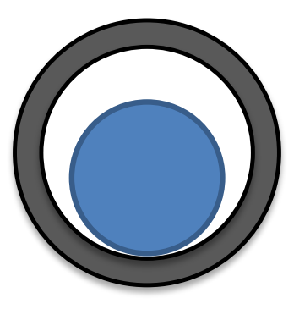
Main challenge for Si-based anodes:
Volume changes during cycling process

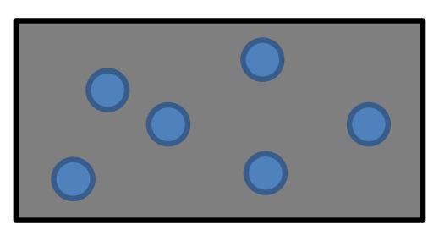
→ Degradation, fracture, loss of contact
→ Additional SEI formation
→ Capacity fading

Basic building blocks → **Advanced architectures**

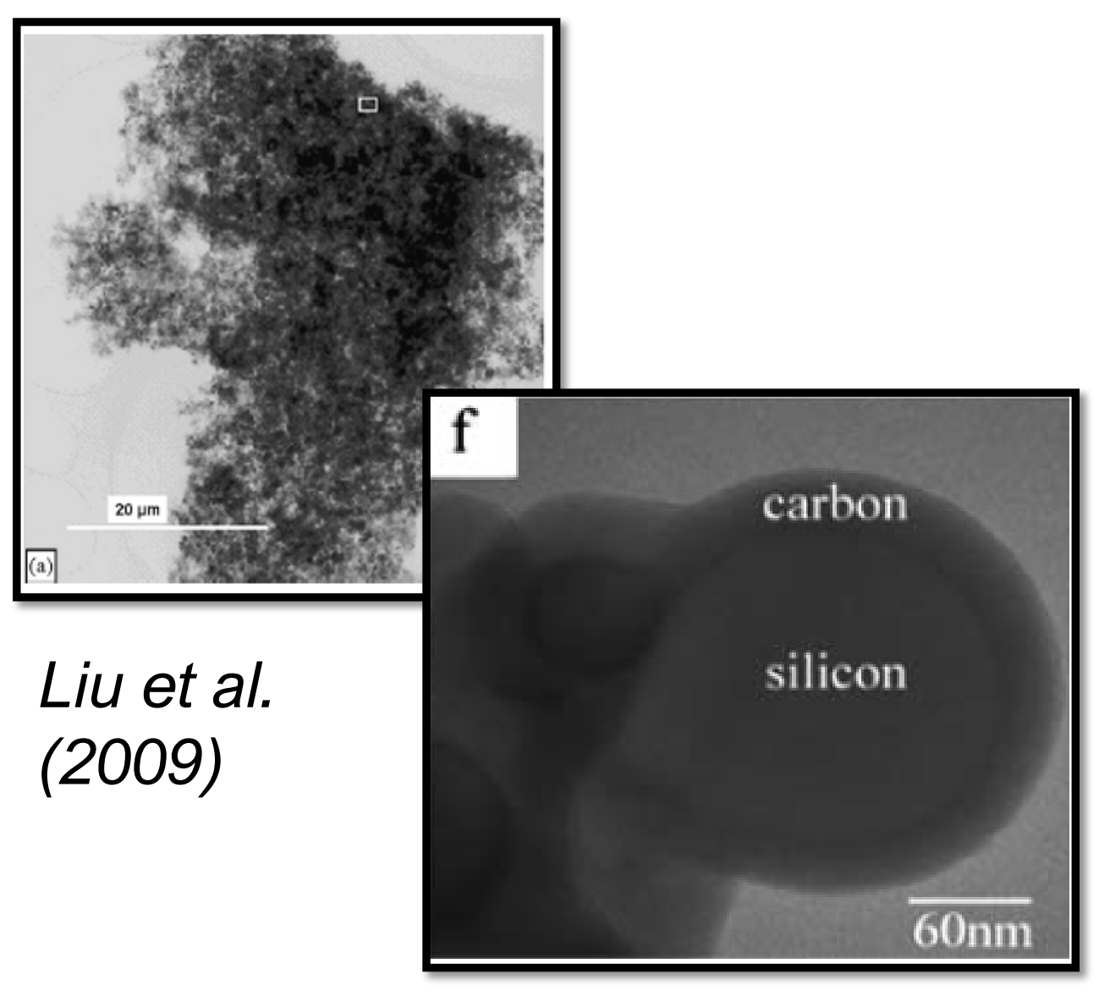

Nanoparticles


Core-shell coatings

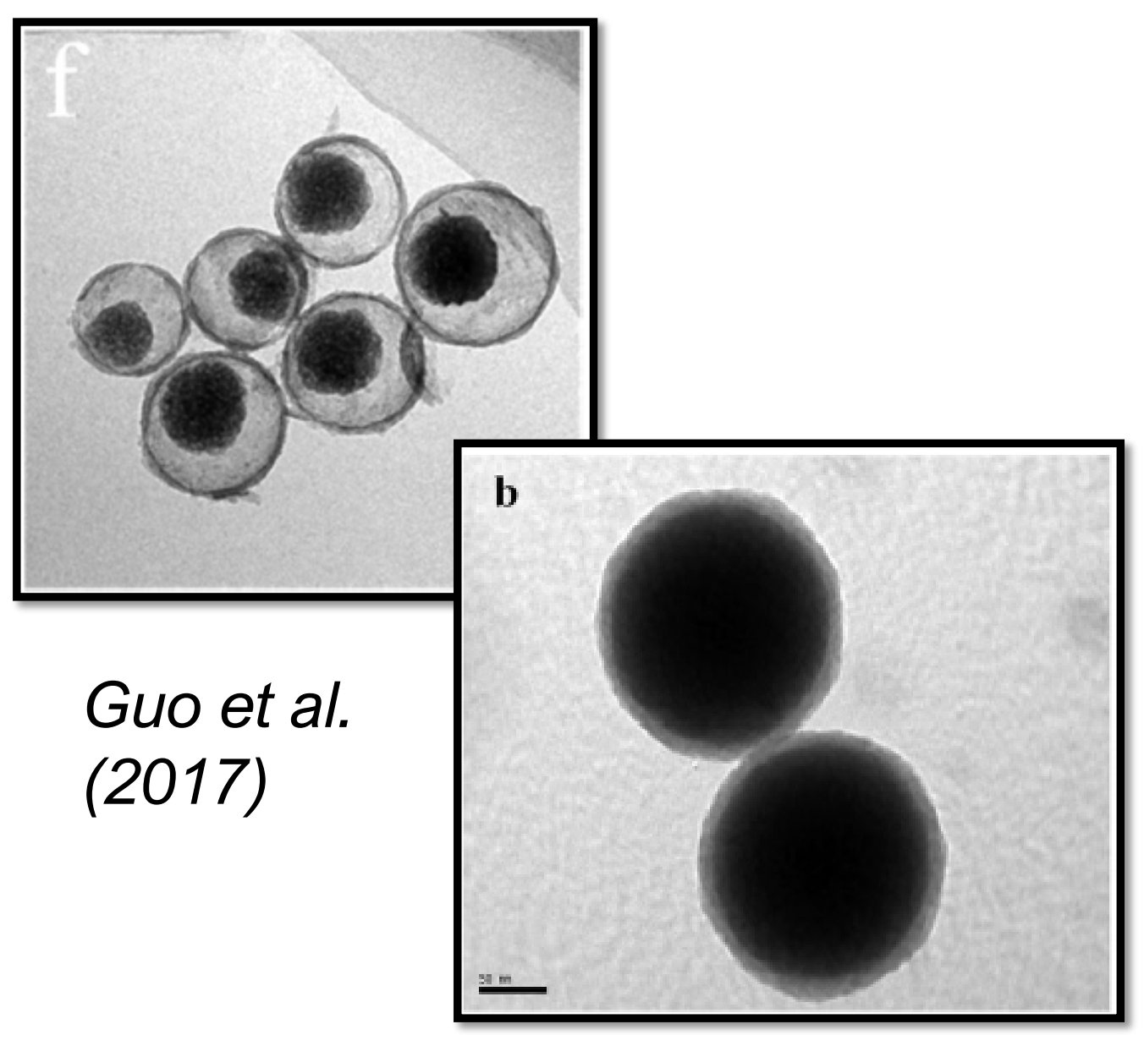

Yolk-shell particles


Composite matrix

Wet-chemical synthesis routes towards carbon coatings:

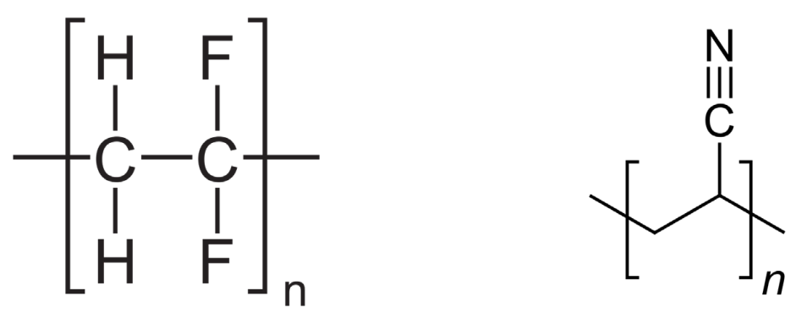


Liu et al. (2009)
Xu et al. (2010)



Guo et al. (2017)
Fuertes et al. (2012)

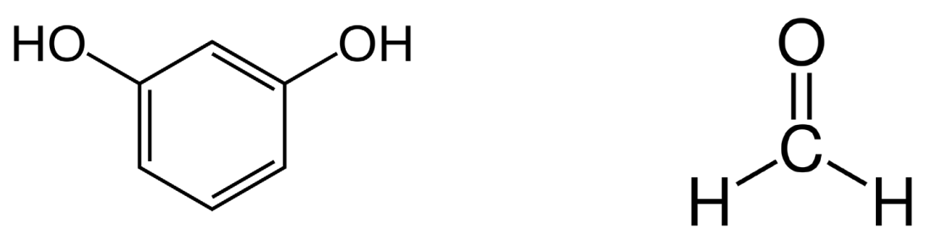
Polymers (thermal decomposition):



- PVDF or PAN polymer powder
- Dissolve in NMP
- Drying step + thermal decomposition

→ Coated Si particles
→ Nanocomposite matrix

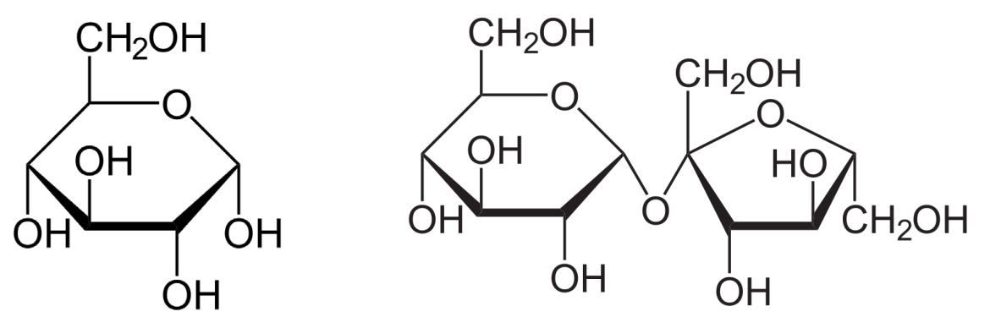
Resorcinol-formaldehyde (hydrothermal route):



- Water/ethanol mixed solution under hydrothermal conditions
- Final thermal processing step

→ Hard carbon shells
→ Possible etching towards hollow structures

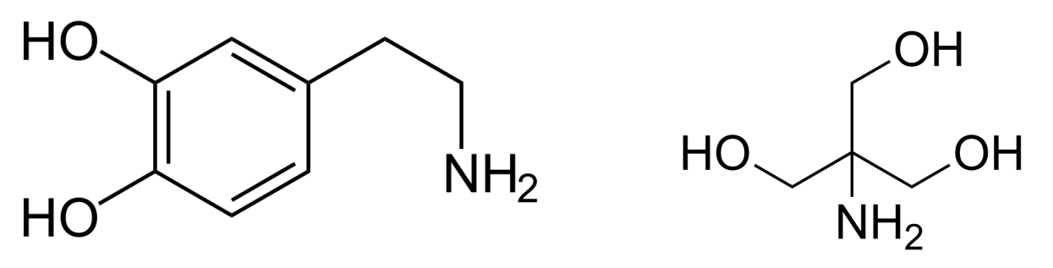
Sugars (hydrothermal route):



- Aqueous solution under hydrothermal conditions
- Final thermal processing step

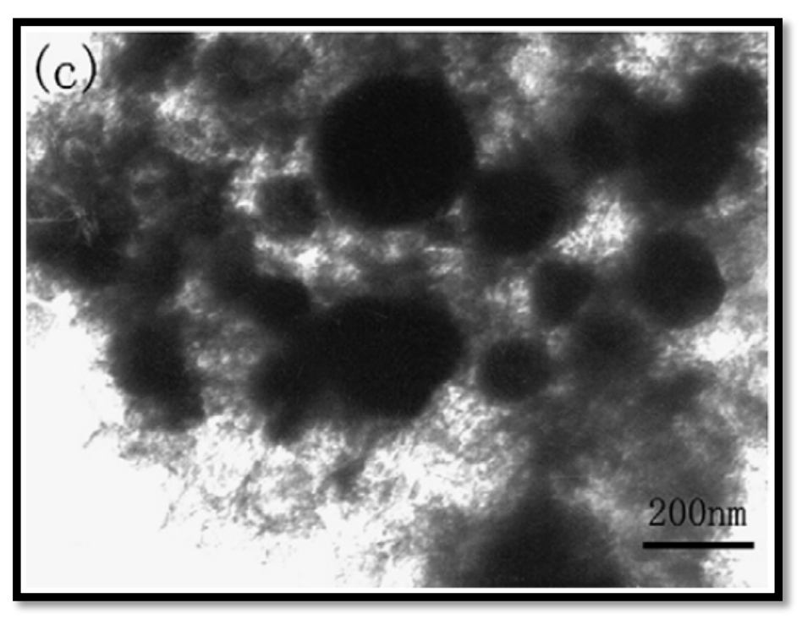
→ Glucose: loose cotton-like structure
→ Sucrose: hard-carbon coating

Dopamine (thermal decomposition):

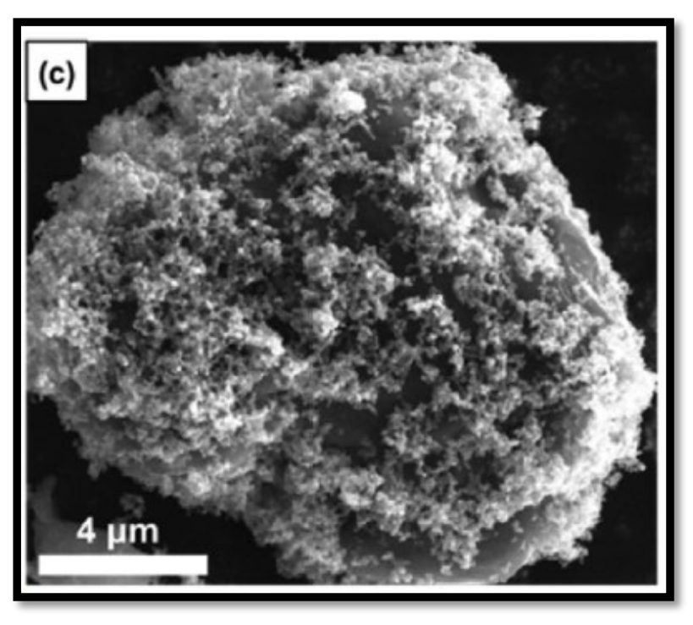


- Dopamine.HCl + Tris dispersion
- Thermal decomposition after polydopamine coating formation

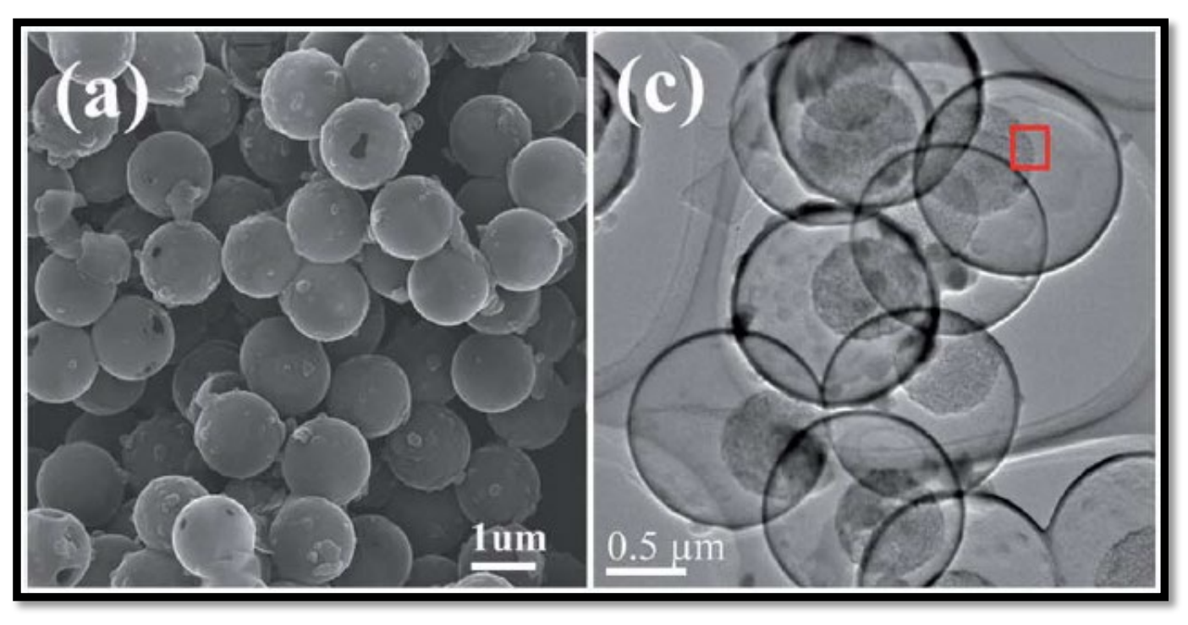
→ Hard carbon shells
→ Possible etching towards hollow structures



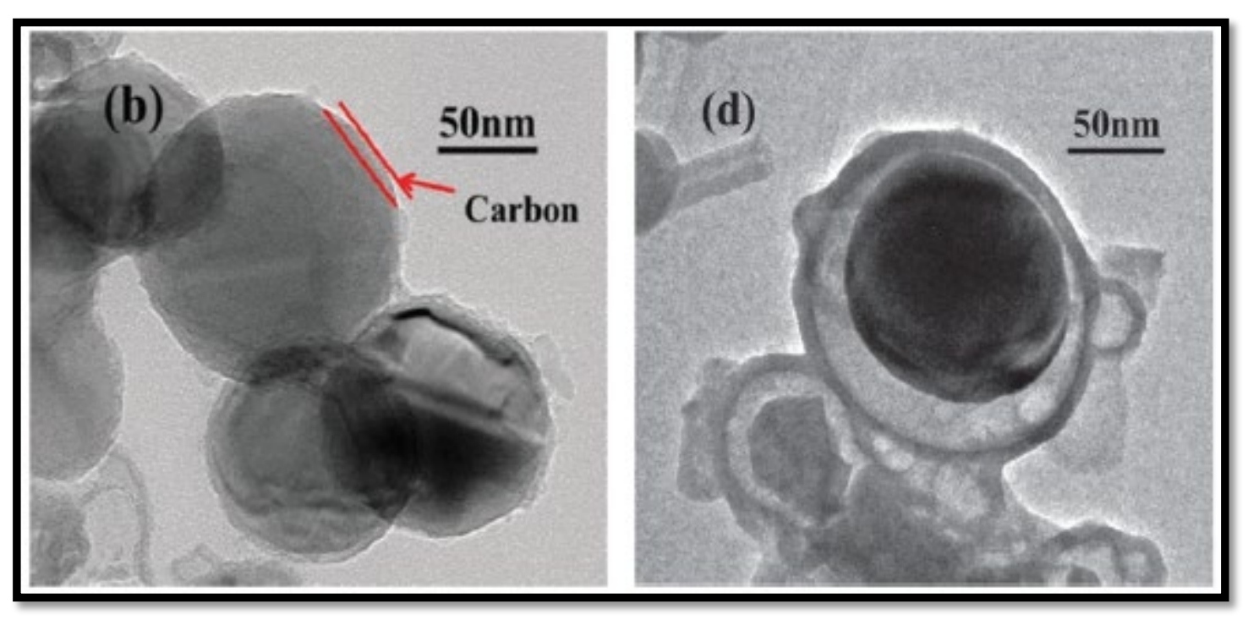
Wang et al. (2007)



Jeong et al. (2016)



Ru et al. (2013)

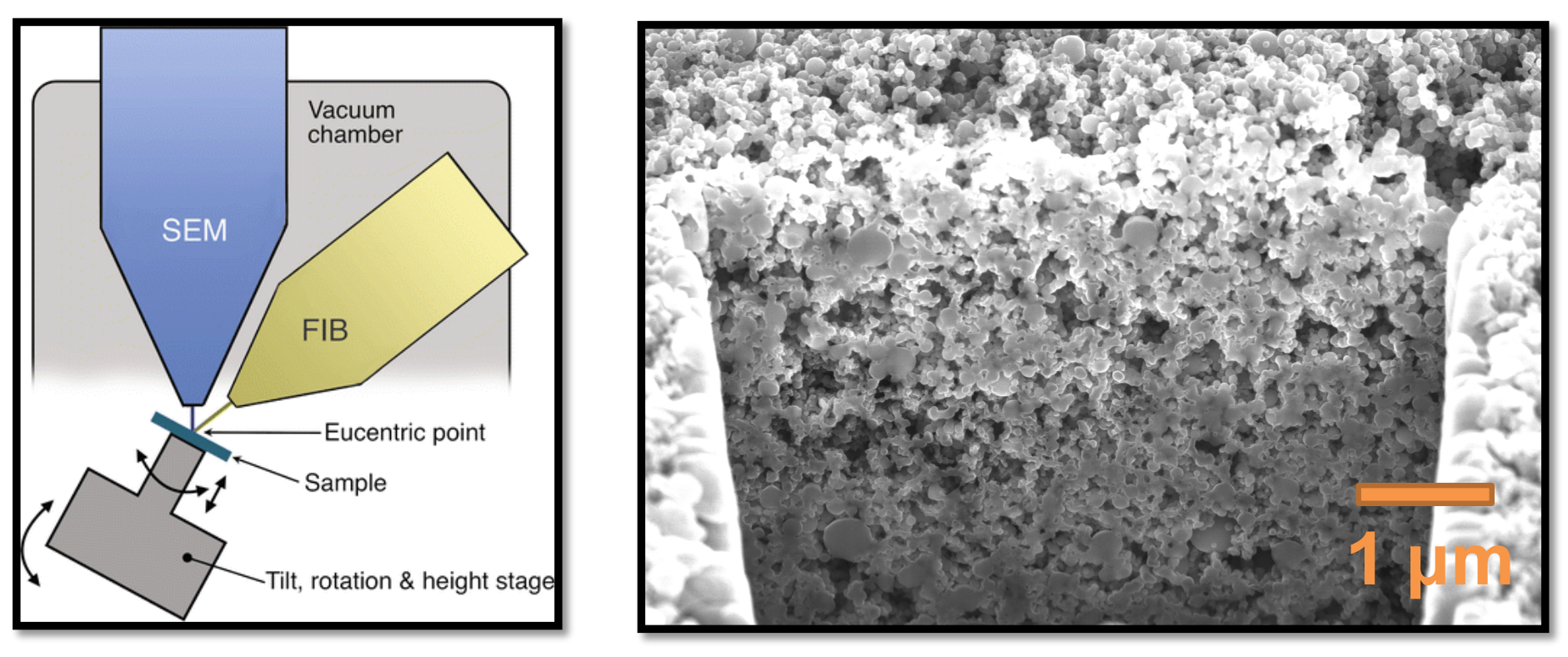


Pan et al. (2014)

Advanced characterization of composite structures and interfaces:

Focused Ion Beam (FIB)-SEM:

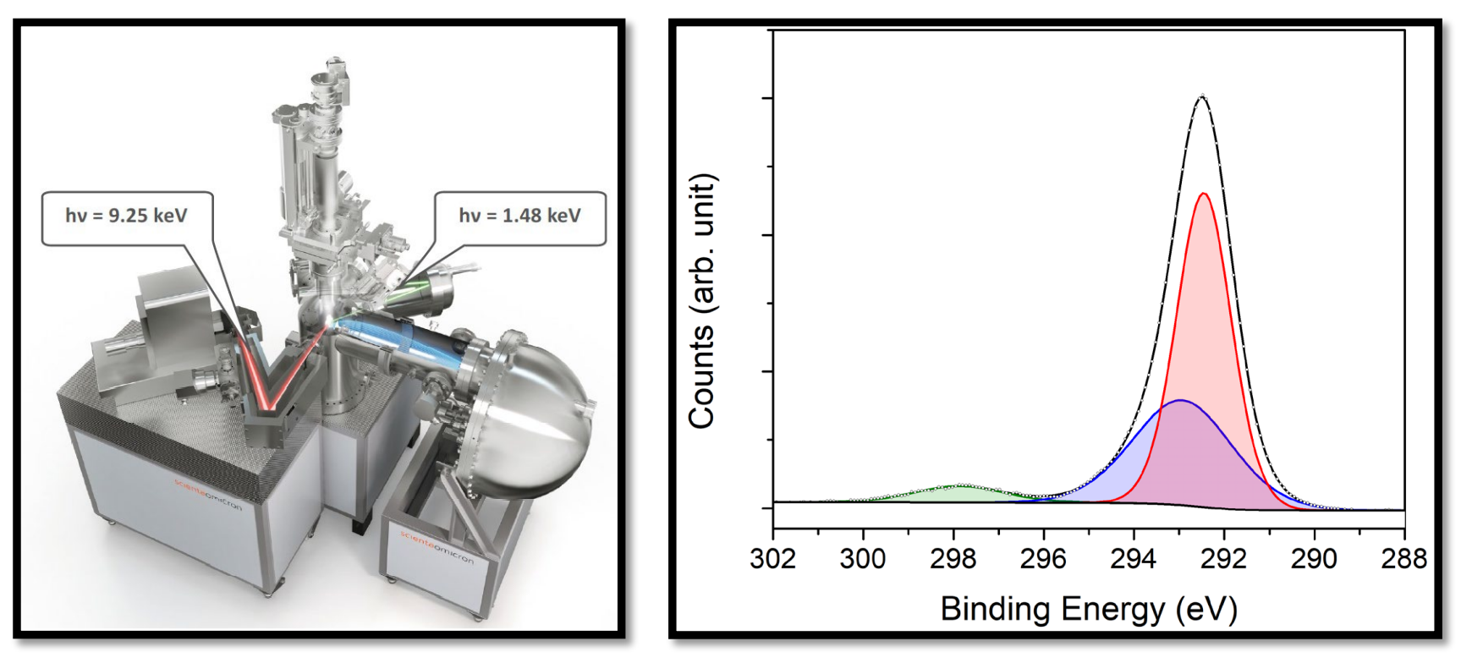
- Dual beam setup alongside SEM
- FIB: Ga-ion source for sputtering/milling
- Used for making cross sections and shaping on nm-µm scale
- Cross-sectional morphology and imaging of electrodes and battery stacks



Brüggeman et al. (2014)

Hard X-ray photoelectron spectroscopy (HAXPES):

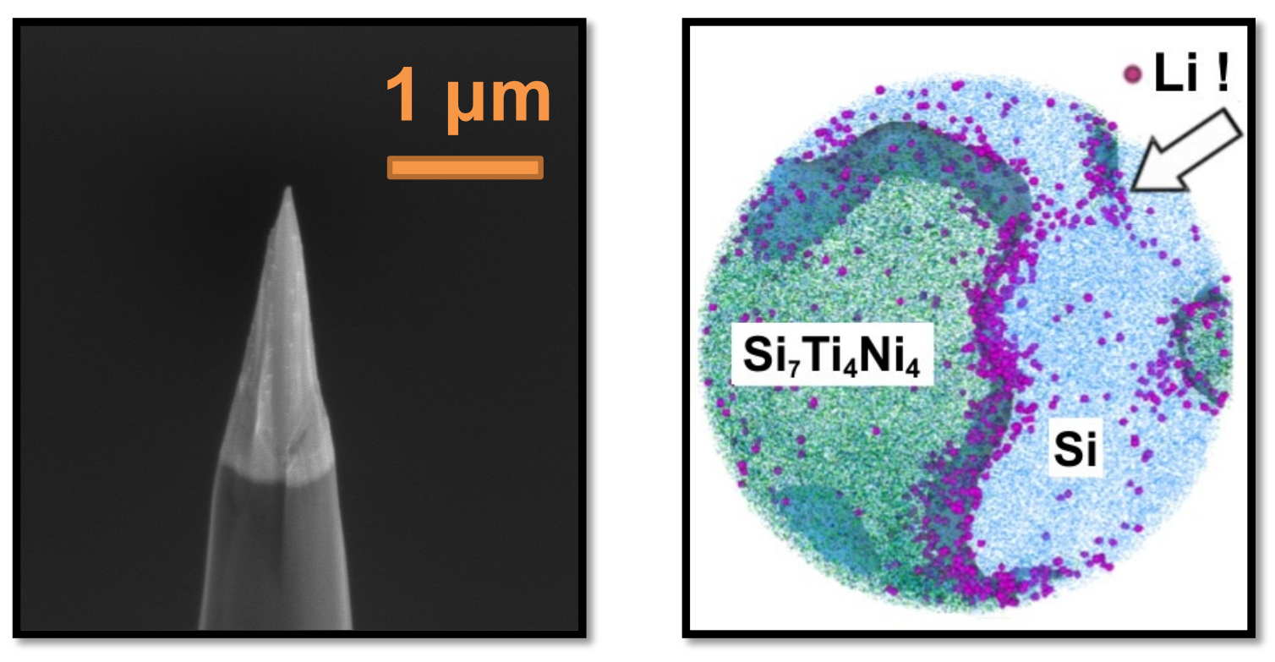
- Lab scale HAXPES setup
  → Normally requires synchrotron!
- Combines Al K_α source (1,48 keV) with Ga K_α source (9,25 keV)
- Increased depth of information:
  → XPS: ~1-5 nm
  → HAXPES: ~30-50 nm



https://www.scientaomicron.com (2019)

Atom probe tomography (APT):

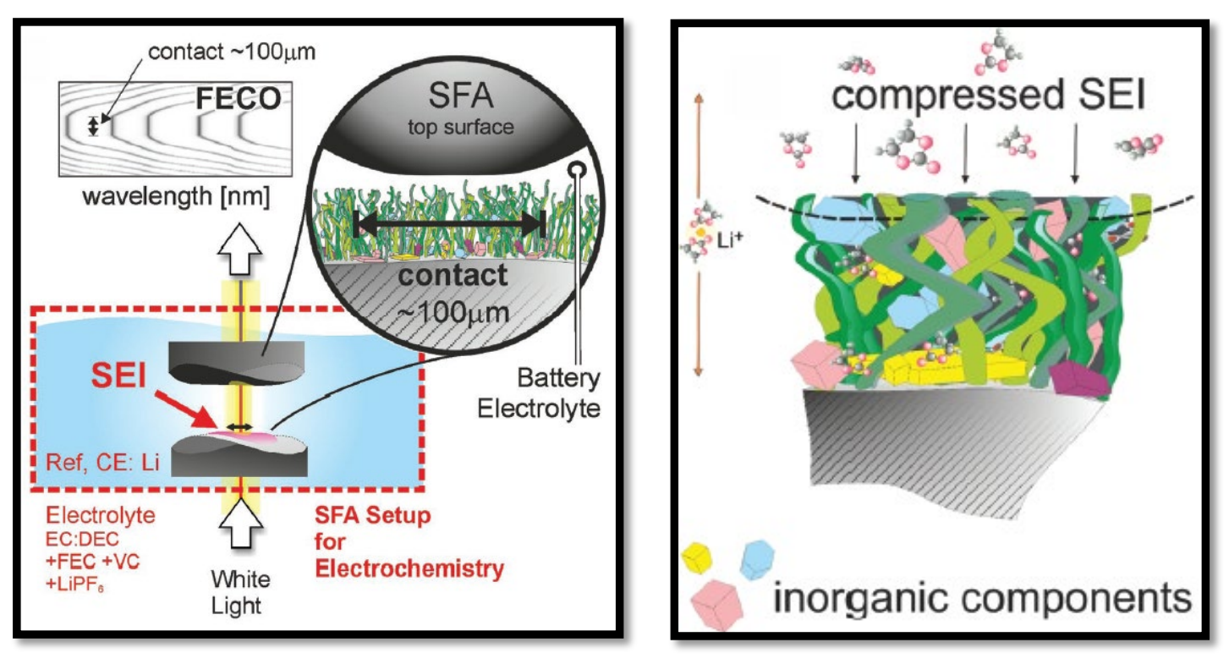
- Combines:
  → Field-ion microscopy (position)
  → ToF mass spectrometry (m/z)
- Field evaporation: voltage or laser pulse
- Sample tip is shaped as needle via FIB
- Atomic-scale 3D-reconstruction



Zheng et al. (2015)

Surface force apparatus (SFA):

- Enables in-situ mechanical analysis of the nanoscopic solid electrolyte interphase (SEI)
- Contact area of 10s of µm with an absolute Å-level height measurement
- Electrochemical environment



Moeremans et al. (2016 and 2019)

References:

[Synthesis section]: Liu, Y.; Wen, Z. Y.; Wang, X. Y.; Hirano, A.; Imanishi, N.; Takeda, Y., Electrochemical behaviors of Si/C composite synthesized from F-containing precursors. J. Power Sources 2009, 189 (1), 733-737. Xu, Y. H.; Yin, G. P.; Ma, Y. L.; Zuo, P. J.; Cheng, X. Q., Nanosized core/shell silicon@carbon anode material for lithium ion batteries with polyvinylidene fluoride as carbon source. Journal of Materials Chemistry 2010, 20 (16), 3216-3220. Guo, S. C.; Hu, X.; Hou, Y.; Wen, Z. H., Tunable Synthesis of Yolk-Shell Porous Silicon@Carbon for Optimizing Si/C-Based Anode of Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2017, 9 (48), 42084-42092. Fuertes, A. B.; Valle-Vigon, P.; Sevilla, M., One-step synthesis of silica@resorcinol-formaldehyde spheres and their application for the fabrication of polymer and carbon capsules. Chem. Commun. 2012, 48 (49), 6124-6126. Wang, Z.; Tian, W. H.; Liu, X. H.; Yang, R.; Li, X. G., Synthesis and electrochemical performances of amorphous carbon-coated Sn-Sb particles as anode material for lithium-ion batteries. J. Solid State Chem. 2007, 180 (12), 3360-3365. Jeong, S.; Li, X. L.; Zheng, J. M.; Yan, P. F.; Cao, R. G.; Jung, H. J.; Wang, C. M.; Liu, J.; Zhang, J. G., Hard carbon coated nano-Si/graphite composite as a high performance anode for Li-ion batteries. J. Power Sources 2016, 329, 323-329. Ru, Y. C.; Evans, D. G.; Zhu, H.; Yang, W. S., Facile fabrication of yolk-shell structured porous Si-C microspheres as effective anode materials for Li-ion batteries. Rsc Advances 2014, 4 (1), 71-75. Pan, L.; Wang, H. B.; Gao, D. C.; Chen, S. Y.; Tan, L.; Li, L., Facile synthesis of yolk-shell structured Si-C nanocomposites as anodes for lithium-ion batteries. Chem. Commun. 2014, 50 (44), 5878-5880. [Characterization section] Bruggemann, D.; Wolfrum, B.; de Silva, J. P., Fabrication, Properties and Applications of Gold Nanopillars. Springer-Verlag Berlin: Berlin, 2014; p 317-354. https://www.scientaomicron.com (2019). Zheng, Y., Renner, F.U., (in preparation). Moeremans, B.; Cheng, H. W.; Hu, Q. Y.; Garces, H. F.; Padture, N. P.; Renner, F. U.; Valtiner, M., Lithium-ion battery electrolyte mobility at nano-confined graphene interfaces. Nature communications 2016, 7, 7. Moeremans, B.; Cheng, H. W.; Merola, C.; Hu, Q. Y.; Oezaslan, M.; Safari, M.; Van Bael, M. K.; Hardy, A.; Valtiner, M.; Renner, F. U., In Situ Mechanical Analysis of the Nanoscopic Solid Electrolyte Interphase on Anodes of Li-Ion Batteries. Adv. Sci. 2019, 6 (16), 5.