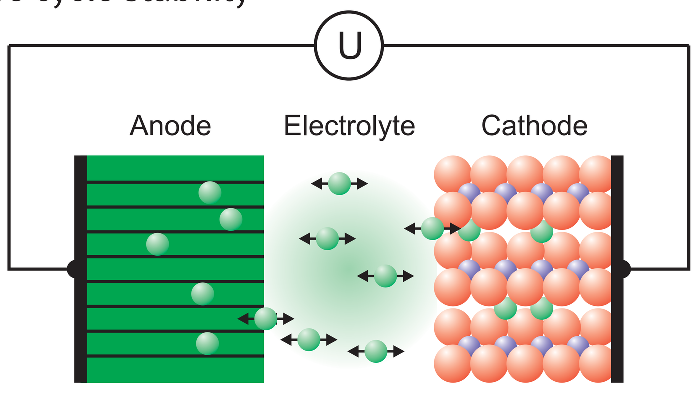
Westfälische Wilhelms-Universität Münster

F. Berkemeier, M. Ibrahim, G. Schmitz
Institute of Materials Physics, Wilhelm-Klemm Str. 10, 48149 Münster, Germany

Intercalation of Lithium in Tin

Introduction

Challenges in lithium ion battery development:
⇒ Increase capacity
⇒ Increase cycle stability



Classical Anode Materials
– Graphite
– Lithium Titanate

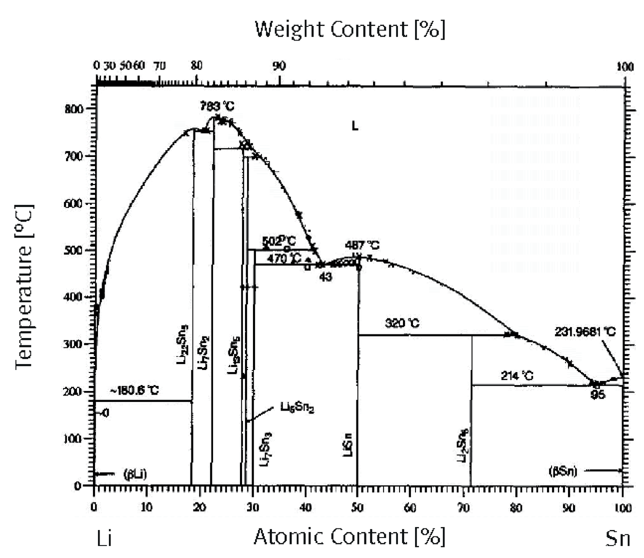
Classical Cathode Materials
– Lithium Cobalt Oxide
– Lithium Iron Phospate

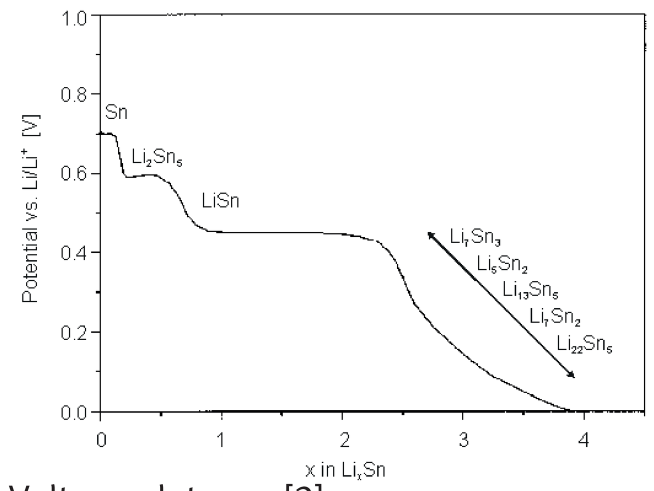
The Lithium-Tin System

Tin shows a much higher capacity for lithium storage than graphite:
– C (Graphite) ~ 300 mAh/g
– C (Tin) ~ 800 mAh/g

But it exhibits a poor cycling stability, due to the large volume expansion and large internal stress during lithium intercalation.

The tin-lithium phase diagram is quite complex, showing 7 intermetallic phases at room temperature [1].

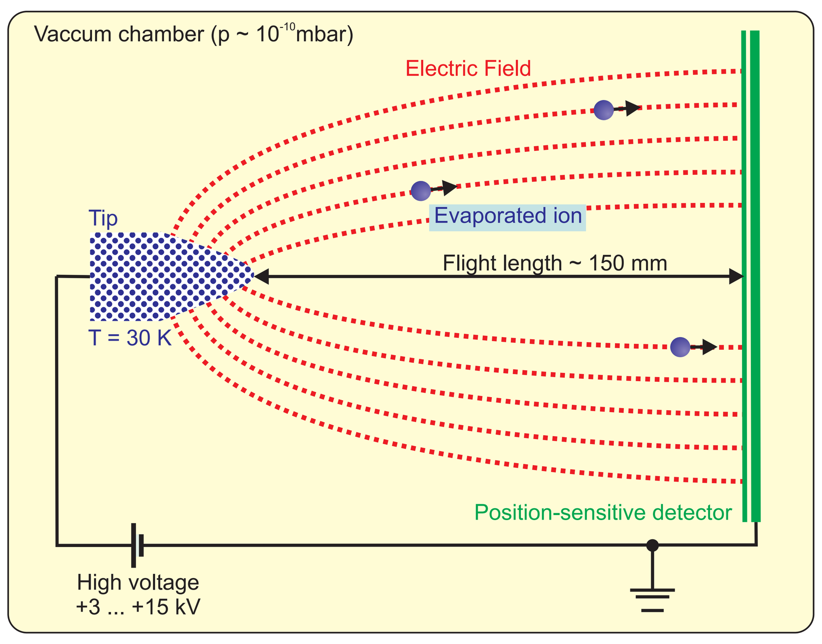




Voltage plateaus [2]
⇒ Chemical potential independent of composition
⇒ Two-phase regions

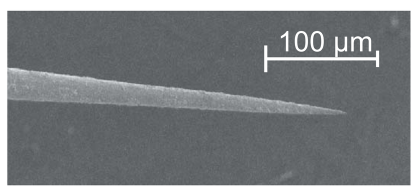
Voltage characteristics can be used to determine the alloy composition!

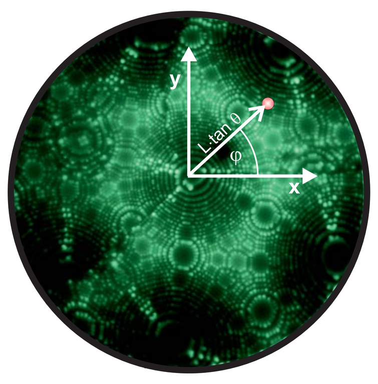
Experimental - Tomographic Atom Probe & Coulometric Titration



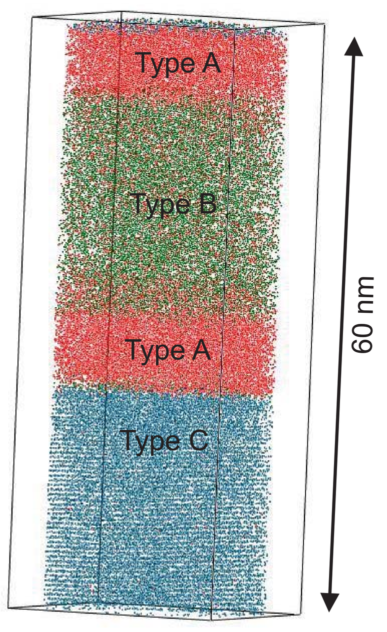
Apex radius ‹ 100 nm
⇒ Very high electricl field strengh at the apex
⇒ Field evaporation of surface atoms

SEM image of a tin tip





Detector image

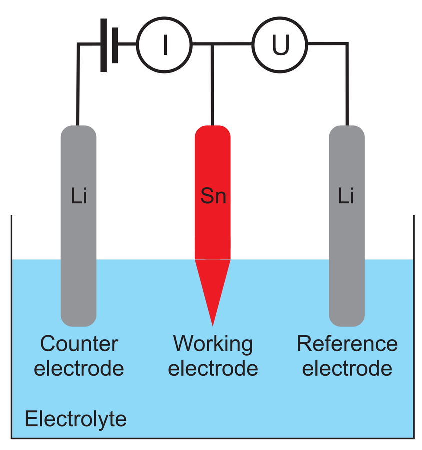


Time of flight measurement
⇒ Identification of individual atoms

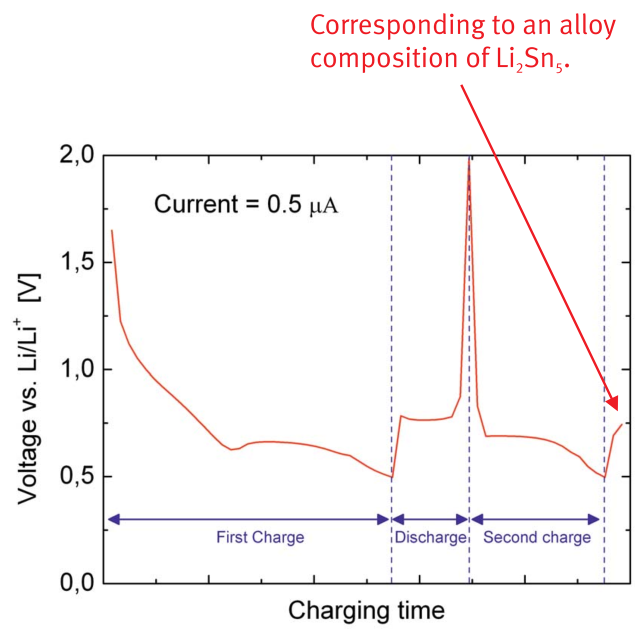
Time-resolved, position-sensitive detection
⇒ 3D atomic reconstruction of the tip

The tin tips are charged versus a lithium counter electrode, using a constant current of 0.5 µA. Simulataneously, the voltage of the tip is measured versus a lithium reference electrode [3], to in-situ obatain the alloy composition according to the voltage curve.

⇒ Lithium intercalation into the tin tip up to a well-defined alloy composition.



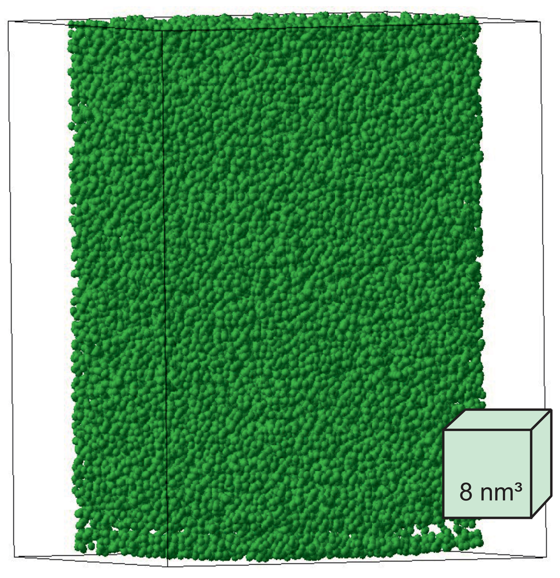
Electrolyte:
DMC/EC (1:1) + 1 mol $LiClO_4$

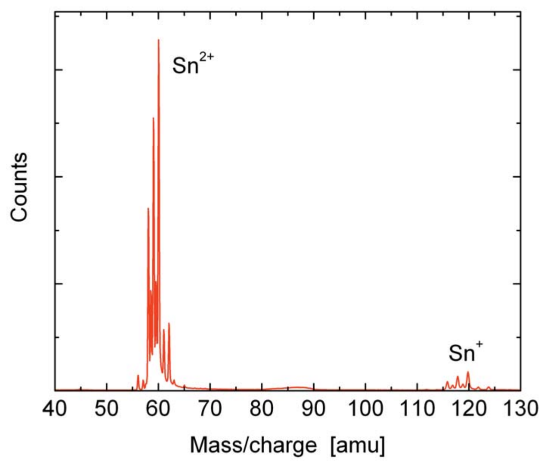


First Results - Pure Tin vs. Lithiated Tin

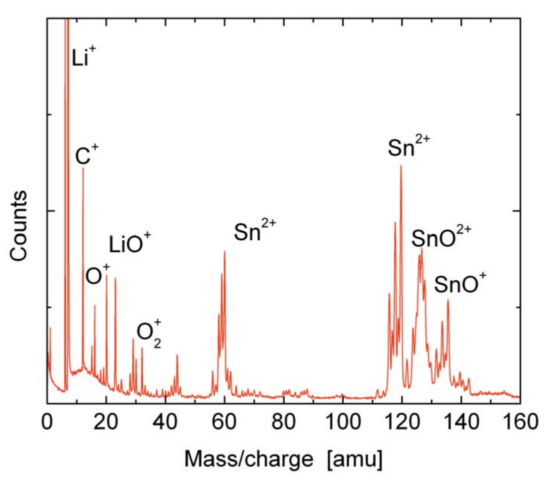
Pure tin has been measured by tomographic atom probe (TAP).

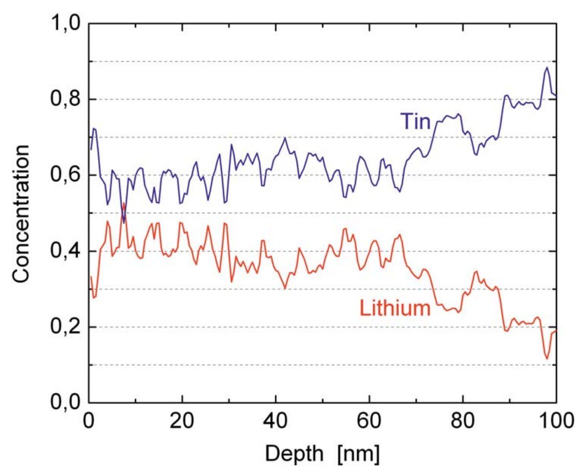
Up to 6.000.000 atoms have been measured before flashing of the tip. In the resulting mass spectrum, all 10 tin isotopes could clearly be identified.

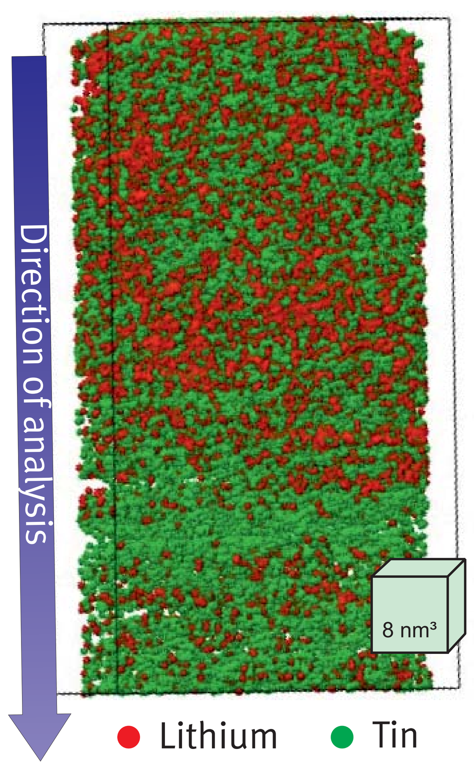




Mass spectrum of a pure tin tip.



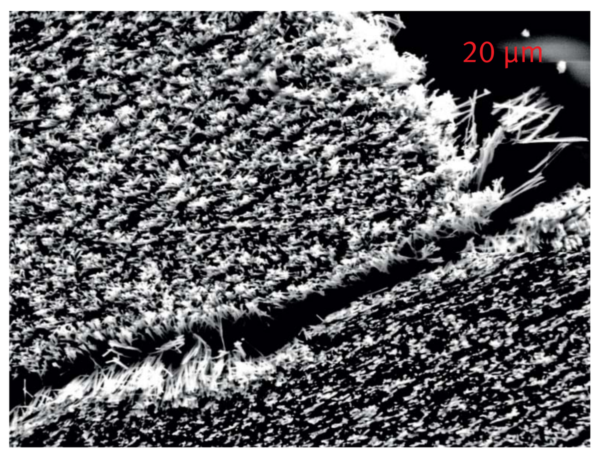


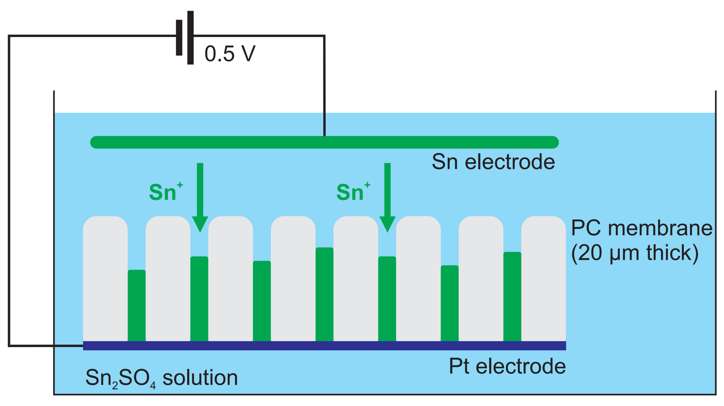


Charged tin, (expected alloy composition: Sn_1Li_1) has been measured by tomographic atom probe. First results show an unexpected, inhomogeneous lithium distribution, with a quite high lithium concentration at the apex of the tip. This high concentration may be due to some SEI layer formation.

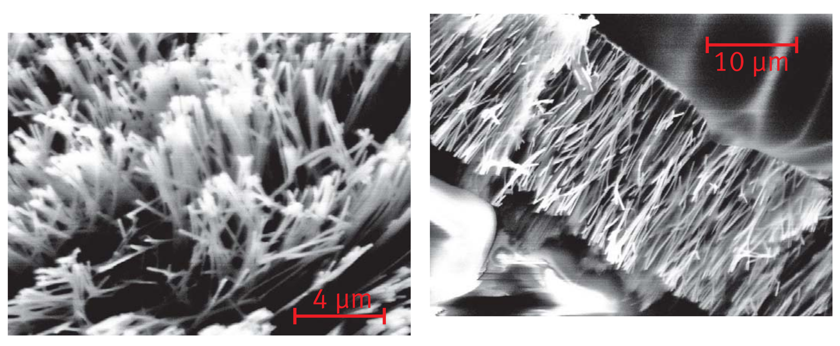
Outlook - Tin Nanowire Arrays

A polycarbonate membrane is deposited onesided by a thin Pt layer and subsequently used as a cathode during an electrolytic Sn deposition, so Sn is deposited in the pores of the membrane. After depostion, the membrane is removed by an organic solvent, resulting in free-standing Sn nano wires.





Membrane thickness = 20 µm
Pore diameter = 100 nm



SEM images of copper nano wires prepared by electrochemical deposition technique.

An analoge preparation of copper nano wires has already been carried out in our group.

⇒ Possible alternative for "classical" TAP tips
⇒ Potential high performance battery electrode, due to large surface area and large free volume

References

[1] Sangster J., Bale C.W., The Li-Sn System, *J. Phase Equilibria*, **19** (1998) 75
[2] Courtney I.A., Tse J.S., Mao O., Hafner J., Dahn J.R., Ab-initio Calculation of the Li-Sn Voltage Profile, *Phy. Rev. B*, **58** (1998) 15583
[3] Schmitz G., Abouzari R., Berkemeier F., Gallasch T., Greiwe G., Stockhoff T., Wunde F., Nanoanalysis and Ion Conductivity of Thin Film Battery Materials, *Z. Phys. Chem.*, **224** (2010)