Lithium Storage Metal Anodes for Lithium Ion Batteries

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Lithium storage metals, such as Si, Al, Sn, Sb, ..., and their alloys (intermetallics) are characterized by extremely high theoretical charge densities and have therefore been investigated as anode materials for rechargeable lithium batteries since the early 1970ies.
This was long before any lithiated carbon materials were considered as anode materials for lithium batteries. Unfortunately, the volume changes related with insertion of lithium in host metals are typically ca. 100 – 200 %, causing crumbling and failure of the active material after a few cycles.

In the 1990ies "second generation" Li-alloy anodes have been proposed by several groups [1]. These anodes were based on thin film or small particle size host metals for Li or on precursor materials such as tin oxides, yielding small particle size host metals after reduction.

In order to overcome the problems with the mechanical disintegration of lithium storage metals and alloys during cycling, several simple strategies have been proposed for the design of the metallic host materials [2-5]:

(i) Proper particle morphology, especially particle size and porosity [1-5]. A nano-structured material shows the same relative expansion as a poly-crystalline material. But the absolute expansions are lower, and hence the cycling stability increases. Pores in the material should offer additional space for expansion and therefore also increase the cycling stability. Nano-structured lithium storage alloys may be prepared either by chemical reduction or by electroplating.

(ii) The incorporation of inactive components in the material. The dilution of the active material with "matrix" components results in an increased cycling stability, since the reacting and expanding phase is stabilized by the non-reacting inactive matrix. This concept was first described in detail by Huggins et al. [6] in the "mixed-conductor matrix concept". The drawback of these composites is that the presence of inactive matrix components reduces the specific charge/charge density of the electrode material.

(iii) The use of multi-phase instead of single-phase materials (e.g., Sn/SnSb instead of pure Sn) [1-5]. In a multi-phase material the single components usually react one at a time. Hence, while one component is reacting (expanding or contracting), the other(s) do(es) not, and can thus stabilize the reacting phase [1-5,7,8].

(iv) The use of components such as "SnSb" which show reversible phase separation and restoration upon the reaction with Li. XRD and TEM investigations [7,8] of SnSb at various stages of charge point to a reaction mechanism where Li_3Sb is formed and in parallel Sn is segregated (which subsequently reacts reversibly with Li). This means, that additional nano-structuring occurs in situ. Furthermore, this mechanism is reversible, which should at least to some extent counteract the aggregation of Sn into larger clusters during cycling (giving rise to problems with cracking and crumbling due to the volume changes).

Despite the drastic improvement of the cycle life of nano-particular multiphase lithium storage alloys compared to conventional host materials, which are based on larger particle size metals, there are still some major problems to be solved to be able to compete with Li-carbon anodes.

As lithium storage alloys and thus the interface to the electrolyte are not dimensionally stable during operation there is some irreversible capacity (= electrolyte decomposition) even after prolonged cycling. Moreover, the Li recovery in the 1st discharge cycle is usually quite unsatisfactory. This problem ist mostly related with unsufficient contacts between the active material and the current collector. The dramatic effect of the morphology of the current collector on the cycling efficiency of Li-alloy anodes has been demonstrated recently for Si on Cu [9].

Furthermore, the strongly expanding anode material is also a challenge to the binder, which has to allow for some volume changes but, on the other hand, has also to maintain the integrity of the electrode.

Strategies to solve the above-mentioned problems by measures like reactive and non-reactive electrolyte additives [10-12] improving the properties of the Solid Electrolyte Interface (SEI) and by choice and distribution of binder materials in composite electrodes [13] will be presented and discussed.

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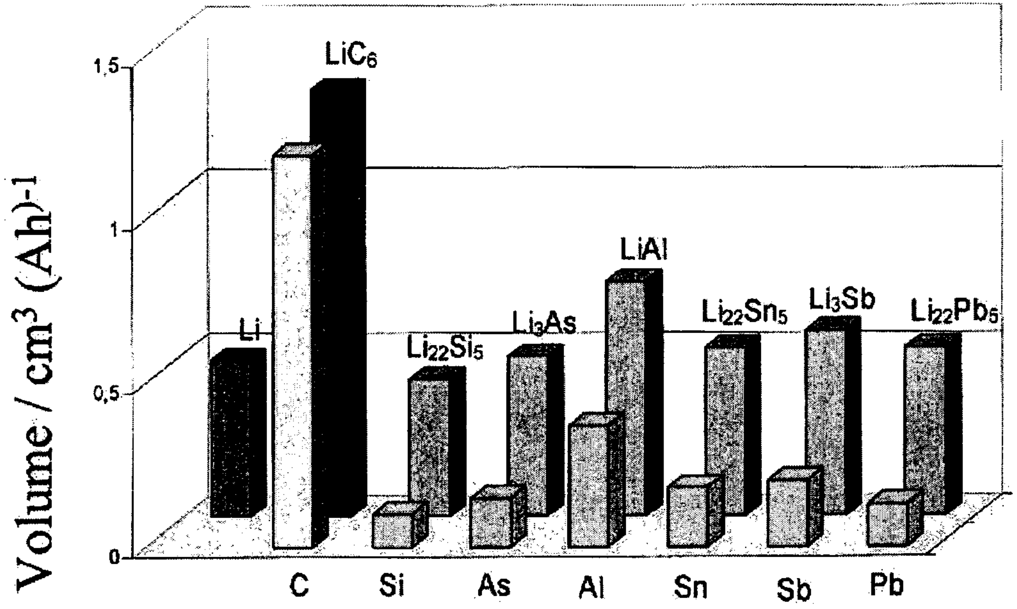
ACKNOWLEDGEMENT

Support by the Austrian Science Funds in the special research program "Electroactive Materials" is gratefully acknowledged.

Lithium Storage Metals

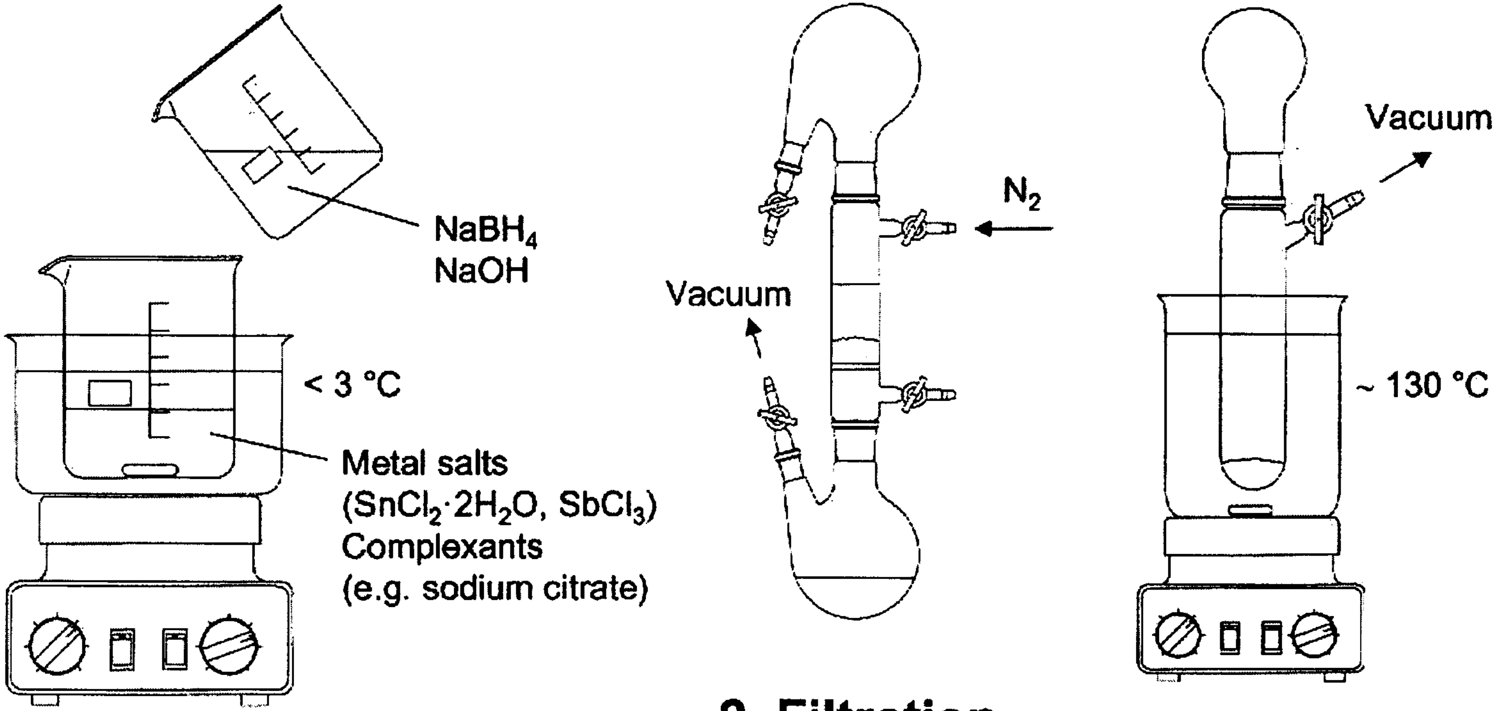
										He
					B	C	N	O	F	Ne
					Al	Si	P	S	Cl	Ar
Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Theoretical Volume Changes During Cycling



(Volumes normalized to 1 mol Li)

Synthesis of Metal and Alloy Powders



$NaBH_4$
$NaOH$

< 3 °C

Metal salts
($SnCl_2 \cdot 2H_2O$, $SbCl_3$)
Complexants
(e.g. sodium citrate)

N_2

Vacuum

Vacuum

~ 130 °C

1. Precipitation

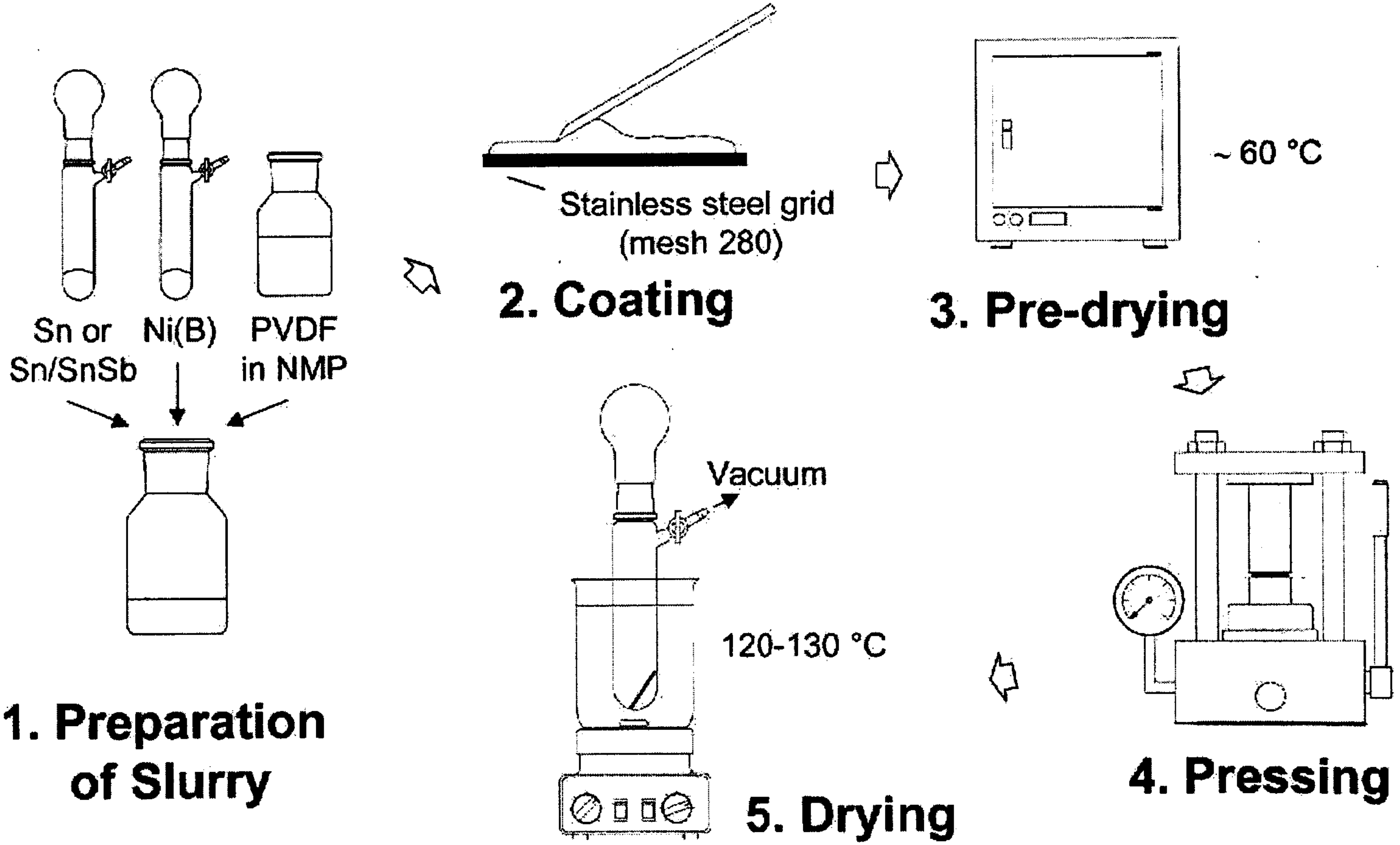
2. Filtration

Washing (H_2O, dil. HCl,
H_2O, acetone)

3. Drying

Storage under Ar

Preparation of Composite Electrodes



Sn or Sn/SnSb

Ni(B)

PVDF in NMP

1. Preparation of Slurry

Stainless steel grid (mesh 280)

2. Coating

~ 60 °C

3. Pre-drying

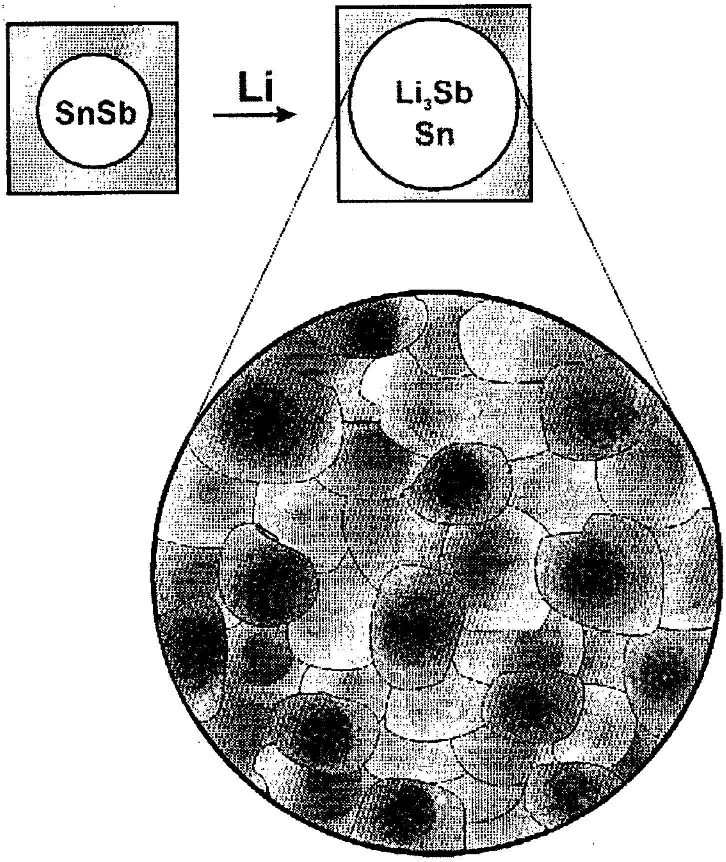
4. Pressing

Vacuum

120-130 °C

5. Drying

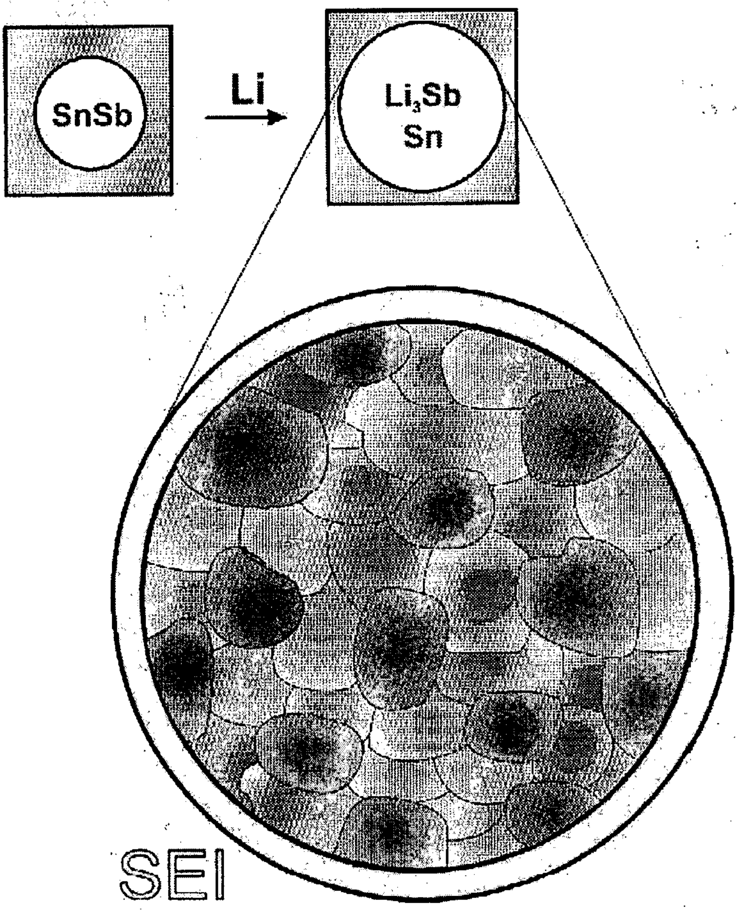
"Mosaic" Structure through Phase Separation



1st step: $SnSb + 3\,Li^+ + 3\,e^- \leftrightharpoons \text{'}Li_3Sb\text{'} + Sn$

2nd step: $Sn + 4.2\,Li^+ + 4.2\,e^- \leftrightharpoons \ldots \leftrightharpoons Li_{4.2}Sn$

"Mosaic" Structure through Phase Separation



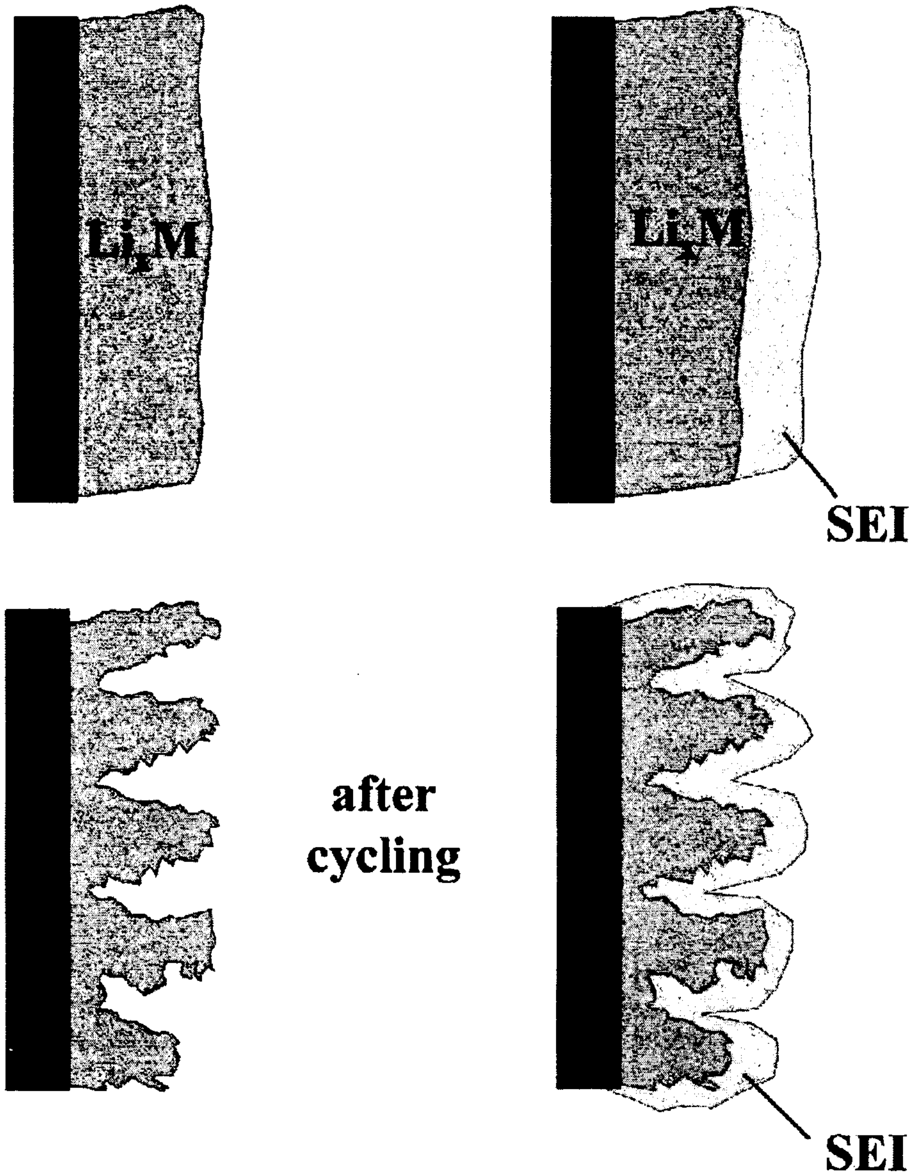
1st step: "SnSb" + 3 Li^+ + 3 e^- ⇆ "Li_3Sb" + Sn

2nd step: Sn + 4.2 Li^+ + 4.2 e^- ⇆ ... ⇆ $Li_{4.2}Sn$

$\mathrm{Li_xM}$ Anodes

Molten Salt

Organic Electrolyte

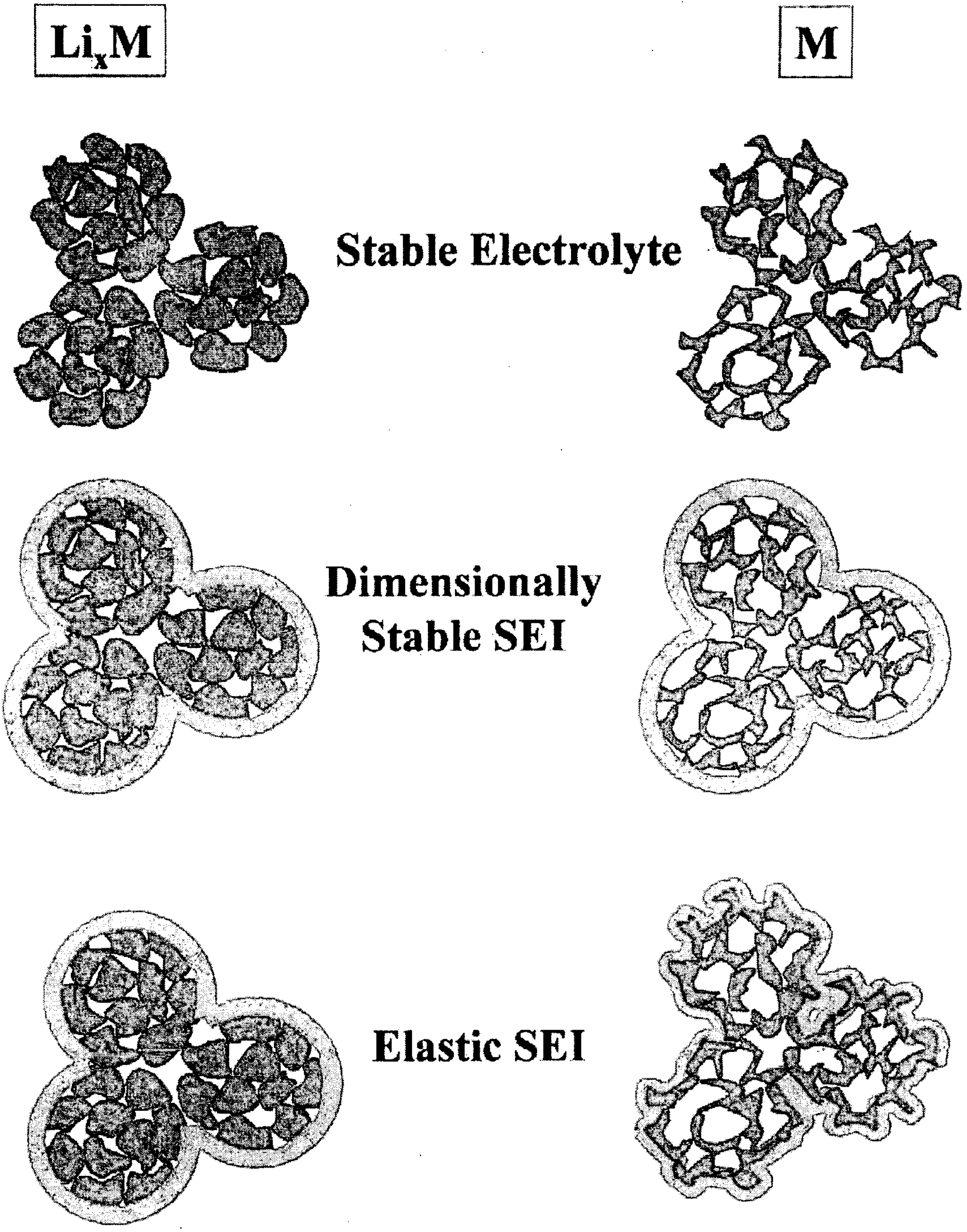


SEI

after cycling

SEI

Wishful Thinking



Li_xM

M

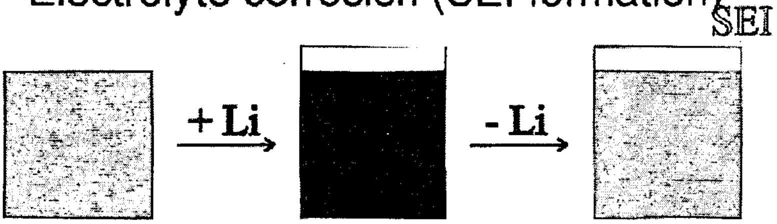
Stable Electrolyte

Dimensionally
Stable SEI

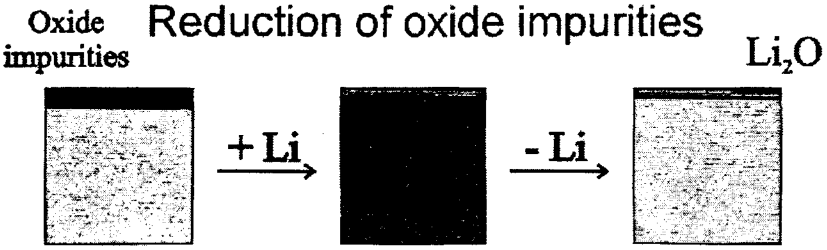
Elastic SEI

Some Reasons for the Irreversible Capacity of Lithium Storage Alloys

Electrolyte corrosion (SEI formation)



Reduction of oxide impurities

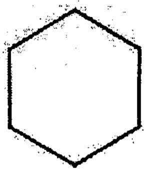


Trapping of Li

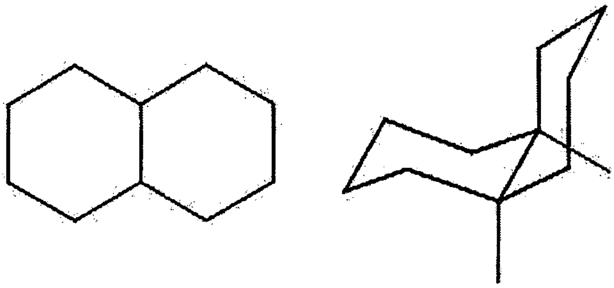
Loss of contact

Non-reactive Surfactant Additives

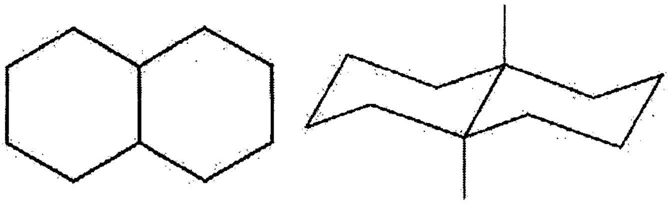
CHex
cyclohexane



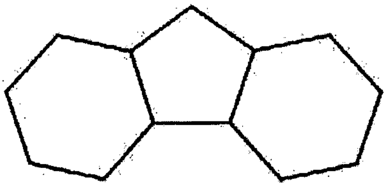
cDec
cis-decalin



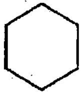
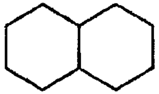
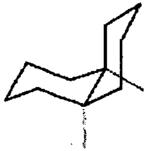
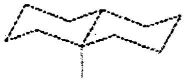
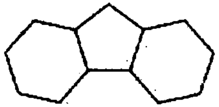
tDec
trans-decalin



PHF
perhydrofluorene

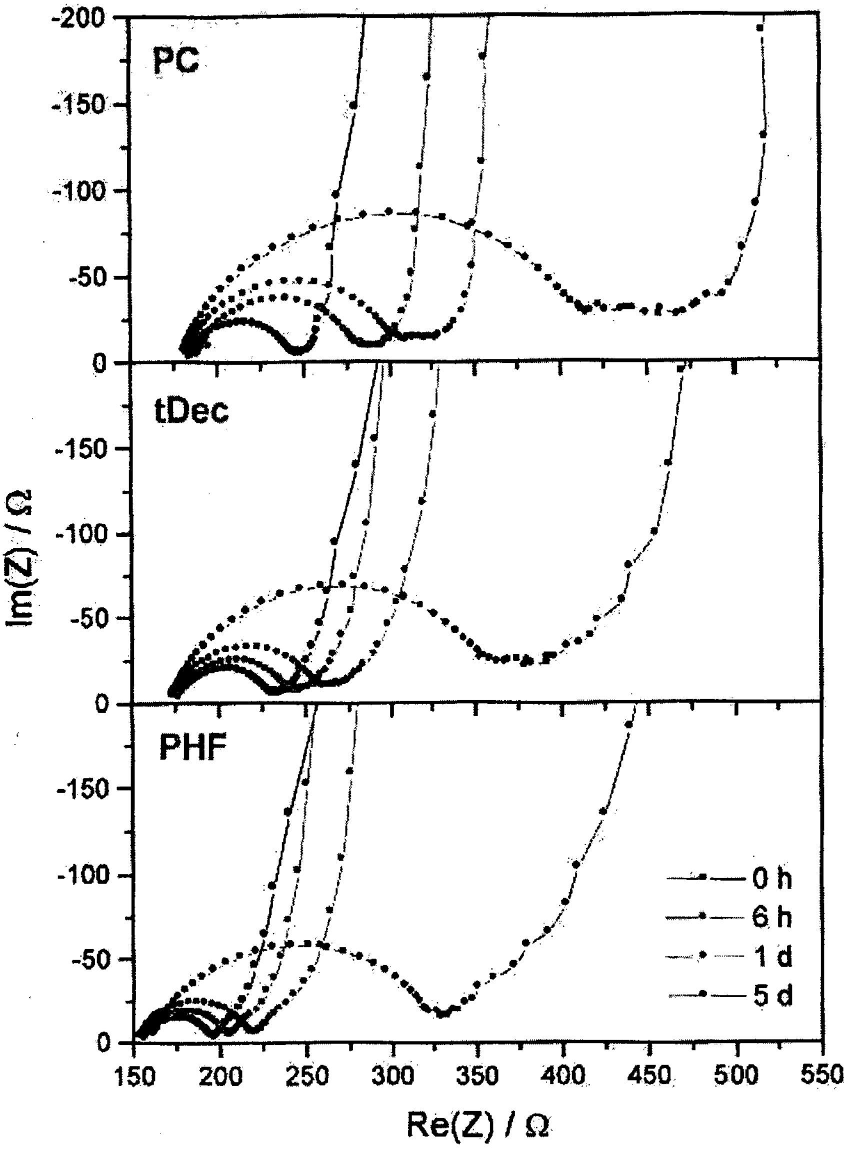


Non-reactive surfactant electrolyte additives

Additive			Solubility in 1 M $LiClO_4$ / PC	Adsorption parameters *
CHex cyclohexane C_6H_{12}				
cDec *cis*-decalin $C_{10}H_{18}$			2.5 - 3.0 wt.%	$\Delta E = 740$ mV $\Delta C = 7.7\ \mu F\ cm^{-2}$ $\Delta G_{ad} = -9.2\ kJ\ mol^{-1}$
tDec *trans*-decalin $C_{10}H_{18}$			2.5 - 3.0 wt.%	$\Delta E = 695$ mV $\Delta C = 7.9\ \mu F\ cm^{-2}$ $\Delta G_{ad} = -9.6\ kJ\ mol^{-1}$
PHF perhydrofluorene $C_{13}H_{22}$			1.0 - 1.5 wt.%	$\Delta E = 930$ mV $\Delta C = 9.8\ \mu F\ cm^{-2}$ $\Delta G_{ad} = -14.0\ kJ\ mol^{-1}$
For comparison: hexadecane $C_{16}H_{34}$				$\Delta E = 565$ mV $\Delta C = 7.1\ \mu F\ cm^{-2}$

* in 0.5 M $LiClO_4$ / PC; J.O. Besenhard, J. Gürtler, P. Komenda, and A. Paxinos; *J. Power Sources* 20 (1987), 253.

Effect of Non-Reactive Surfactant Additives

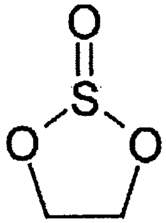


PC: 1 M $LiClO_4$ / propylene carbonate (PC)
tDec: 1 M $LiClO_4$ / PC sat. with *trans*-decalin
PHF: 1 M $LiClO_4$ / PC sat. with perhydrofluorene

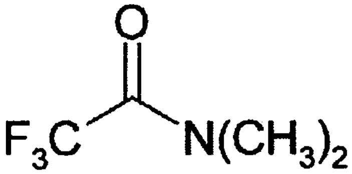
Electrode: Electro-plated nano-structured Sn/SnSb, (geom. area: 38 mm^2)
Pot.static EIS, 1st charge, 100 mV vs. Li/Li$^+$, ampl. = 5 mV, freq. = 100 kHz ÷ 10 mHz

Filming Additives

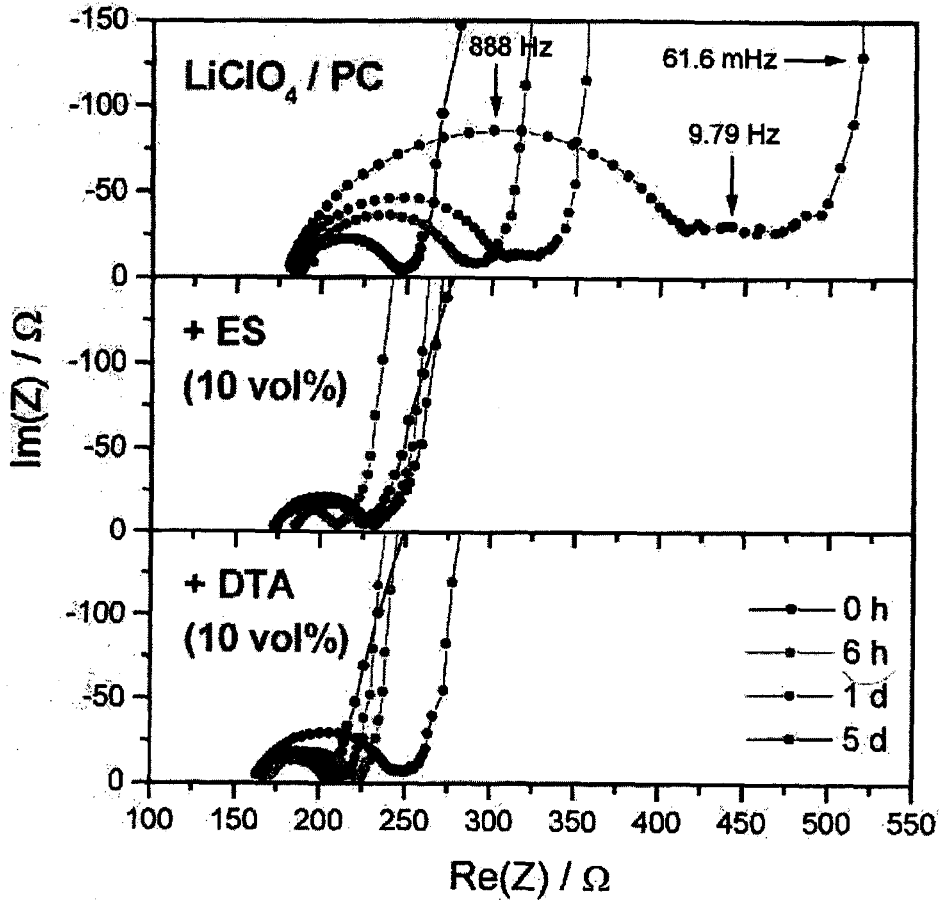
ES
ethylene sulfite



DTA
N,*N*-dimethyl trifluoracetamide



Filming Additives



Sn/SnSb, pot.st. EIS, first charge, 100 mV vs. Li/Li$^+$