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Electrolyte additive investigations: Silicon thin film vs. slurry based composite electrodes

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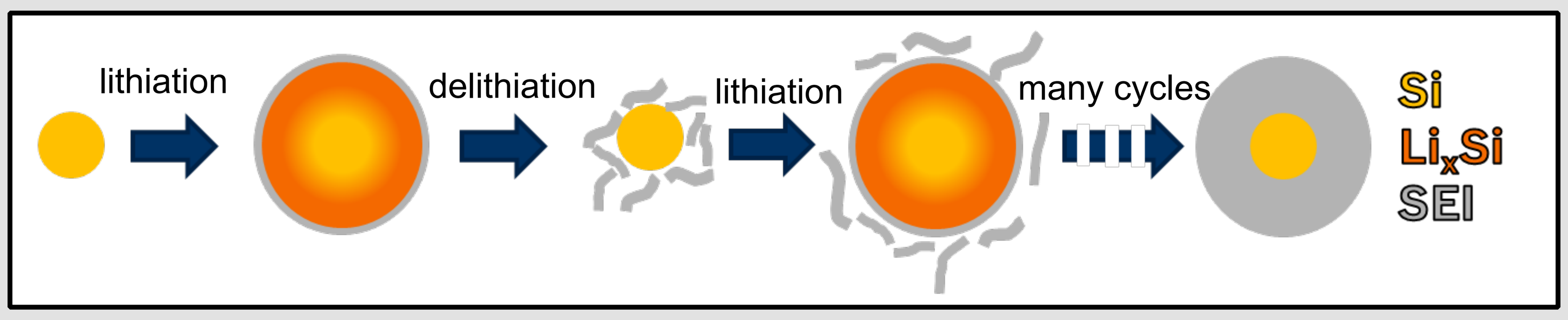
Motivation and theoretical background

Silicon (Si) is a promising candidate to increase the energy density of lithium-ion batteries. However, silicon suffers from fundamental challenge of huge volume changes during cycling which leads to particle breaking and an instable solid electrolyte interphase (SEI).
We present a comparative electrochemical study of several SEI stabilizing electrolyte additives on silicon thin film and slurry based silicon composite electrodes, the latter additionally in full cells. SEI formulation on both electrode types is also studied by X-ray photoelectron spectroscopy (XPS).

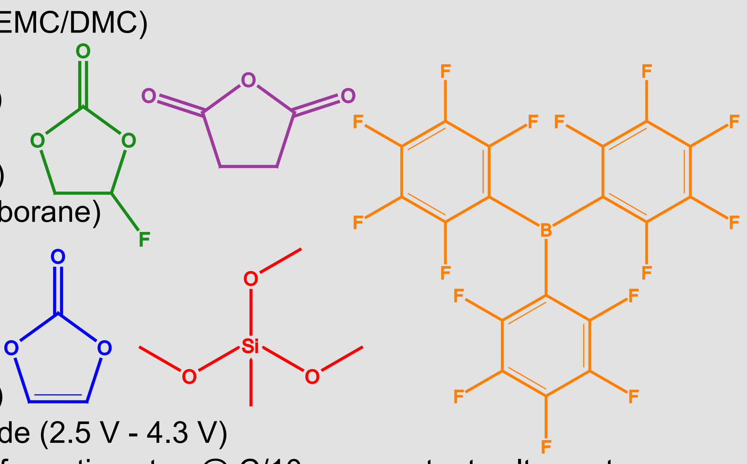


Methods and processes

Materials - electrodes and additives

- Silicon thin films by CVD (t = 50 nm → 70 µAh/cm²)
- Composite electrodes comprising silicon active material, carbon additives and CMC/SBR binder (t = 11 µm → 3 mAh/cm²)
- $Q_{Si,th.}$ = 3579 mAh g^{-1}

- Base electrolyte (1M $LiPF_6$ in EC/EMC/DMC)
- Tested additives:
  - -FEC (Fluoroethylene carbonate)
  - -SA (Succinic anhydride)
  - -TMMS (Trimethoxymethylsilane)
  - -TPFPB (Tris(pentafluorophenyl)borane)
  - -VC (Vinylene carbonate)



Electrochemistry

- CR2016 coin cells
- Half cells vs. Li/Li⁺ (1.5 V - 0.01 V)
- Full cells vs. NCM positive electrode (2.5 V - 4.3 V)
- Galvanostatic cycling @ C/3, one formation step @ C/10, no constant voltage steps
- Graphs show lithiation only

XPS

- PHI Quantera SXM
- $Al_{K\alpha}$ radiation with $h\nu$ = 1486.6 eV
- C-C bonding referenced to 284.8 eV

Additive effects on silicon thin films

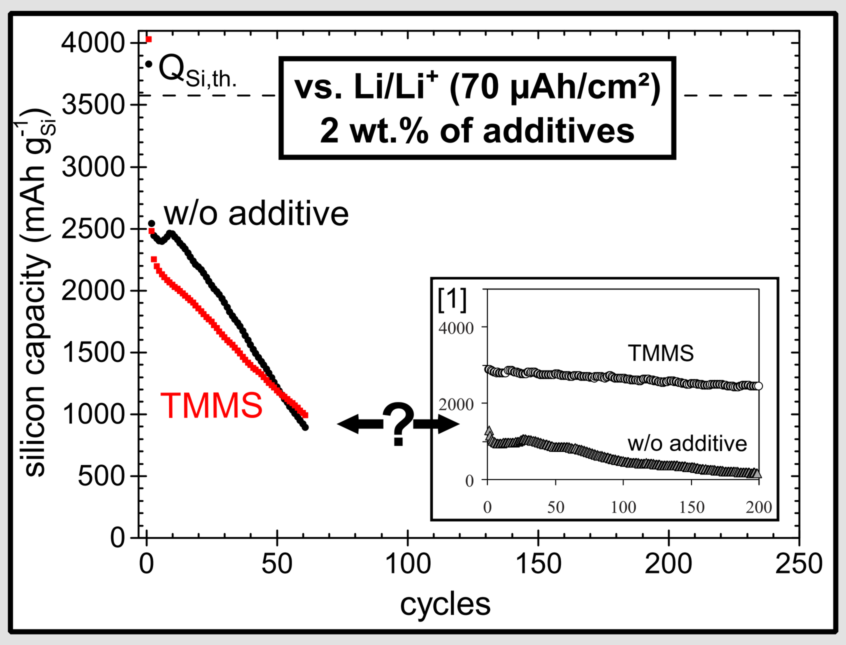


Fig. 1: In contrast to reference [1] TMMS does not improve cyclability. Literature results cannot necessarily be adapted to every system. Comparative study of literature proposed additives required.

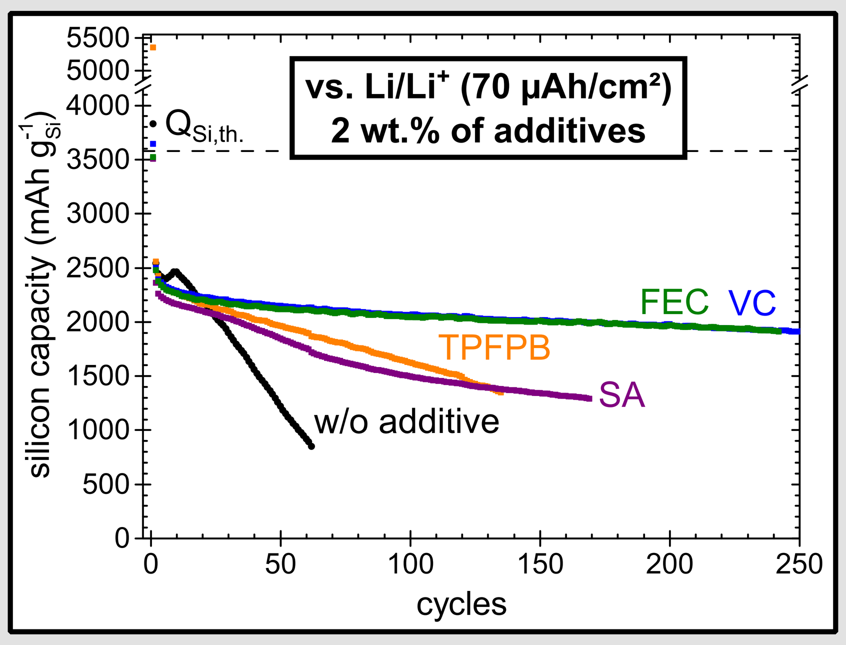
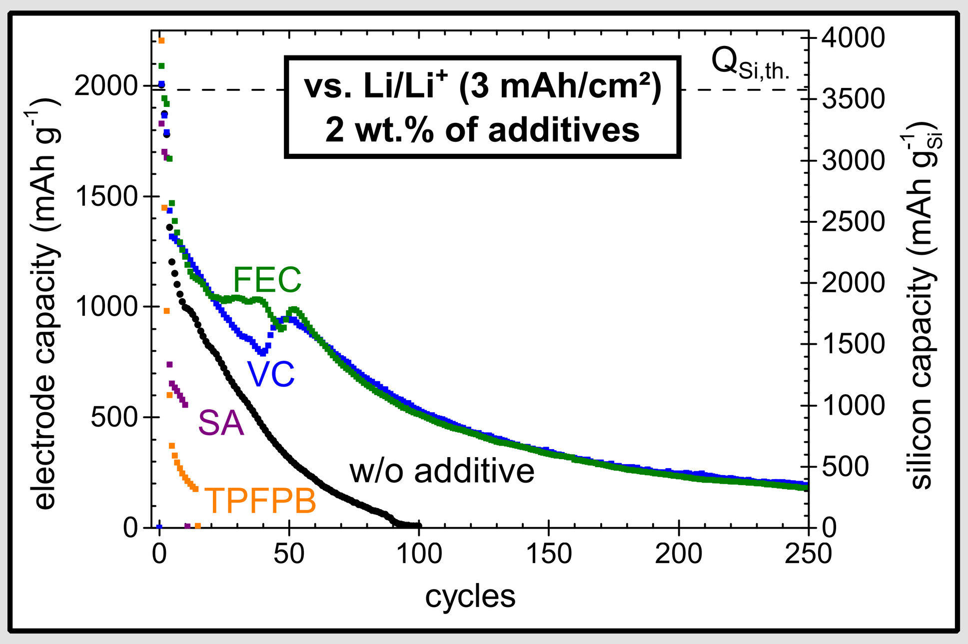


Fig. 2: Additives enhance cycle life. FEC and VC show similar results. TPFPB and SA show faster capacity fade than FEC.

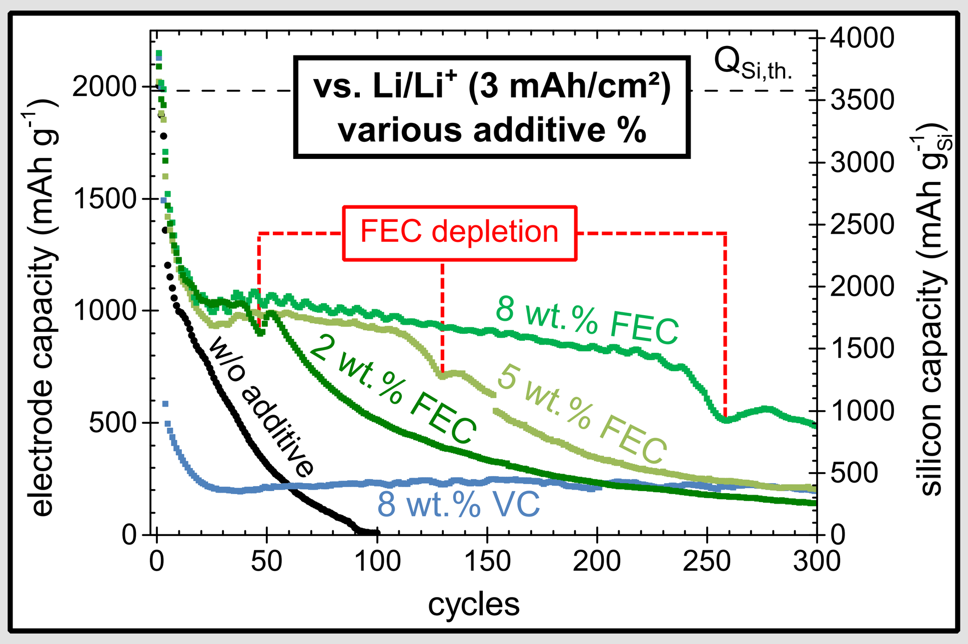
Si thin films are not suitable for electrical vehicles due to their low coverage → higher loadings are inevitably required.

But do Si thin film results hold true for industrial scalable **high loading** composite electrodes? **?**

Additive effects on silicon composite electrodes



Increasing additive amount



Full Cell

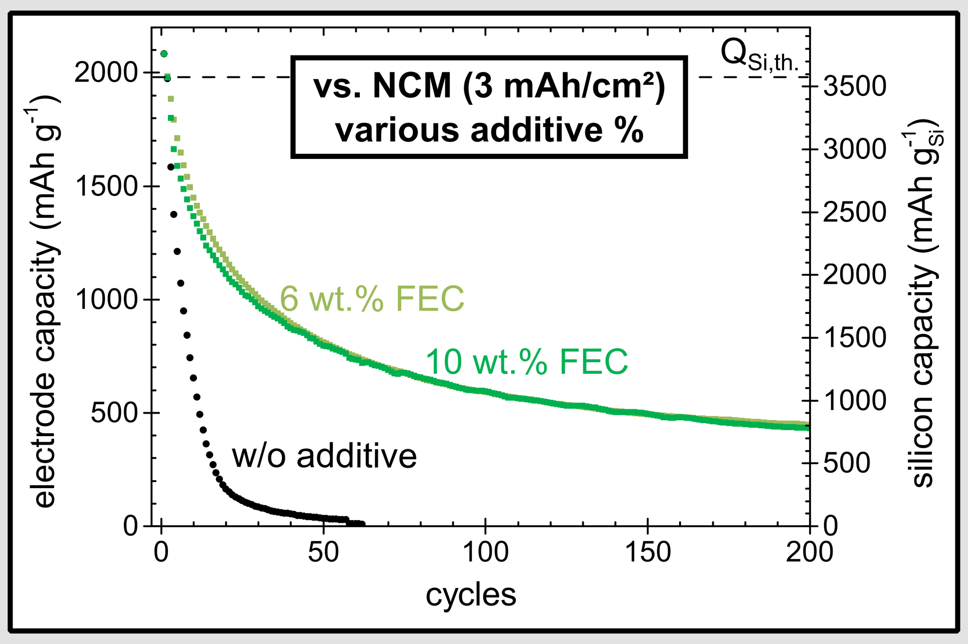


Fig. 3: FEC stabilizes at 1000 mAh/g until cycle 50, followed by fading with slope comparable to base electrolyte. VC fades until cycle 40 with subseqent recovery. SA and TPFPB show a cycle life worsening effect.

→ Can a higher amount of additive extend cycle stability?

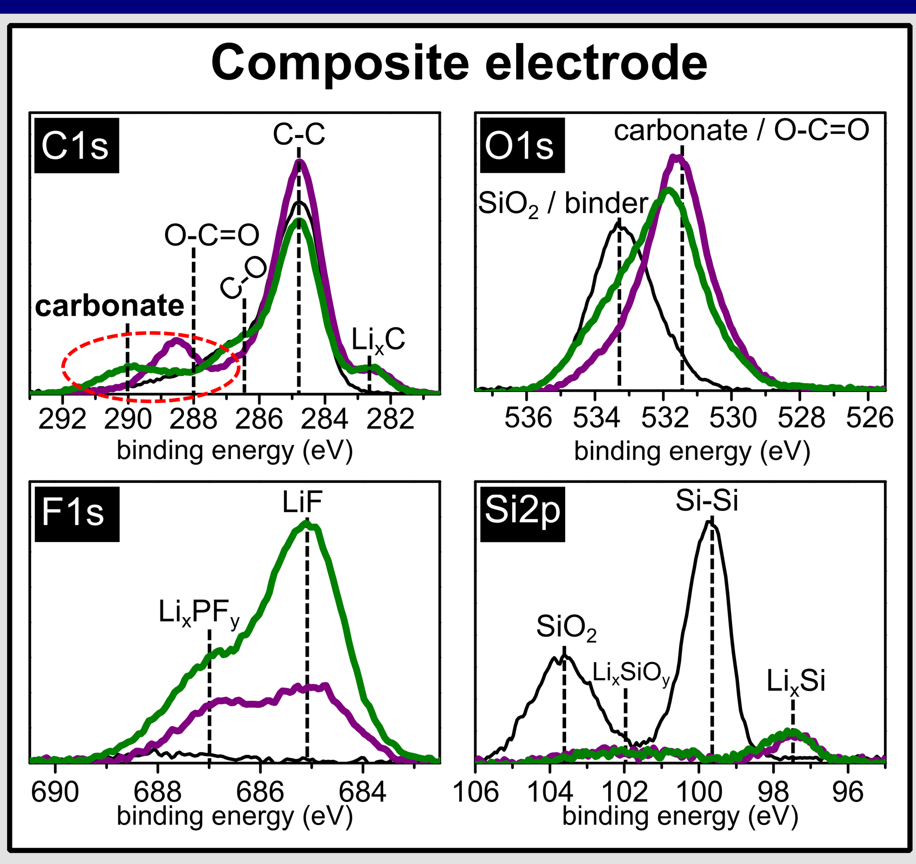
*waves in graph due to temperature variations

Fig. 4: Higher additive concentration results in an increased cyclability in case of FEC, not true for VC. FEC is used in every cycle to mend the SEI. Continuous FEC consumption until FEC depletion, indicated by bumb in graph. Amount of FEC limits cycle life in half cells.

→ Do half cell results hold true for full cells?

Fig. 5: FEC improves cyclability also in full cells. However, continuous fading due to lithium (Li) loss by FEC decomposition in every cycle. Cycle stability in full cells may be limited by Li source and not by FEC amount.

XPS investigations



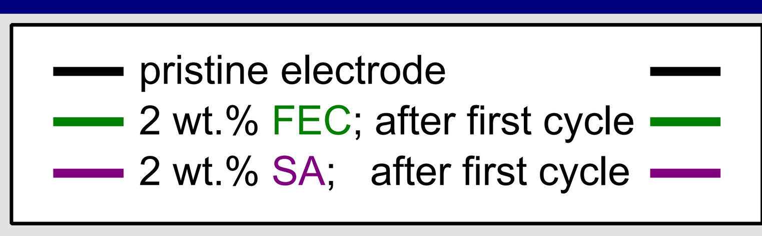


Fig. 6:
C1s: SEI formed in presence of FEC contains more carbonate species.
O1s: Pristine electrode shows peaks resulting from SiO_2 and binder. Peak shift after first cycle for both electrodes due to SEI formation.
F1s: FEC additive decomposition leads to a high amount of LiF in SEI. LiF in "SA electrode" comes only from salt decomposition.
Si2p: Pristine electrode shows peaks resulting from silicon and SiO_2. Peak shift arises due to formation of Li_xSi phase. SEI formation reduces silicon signal intensity.

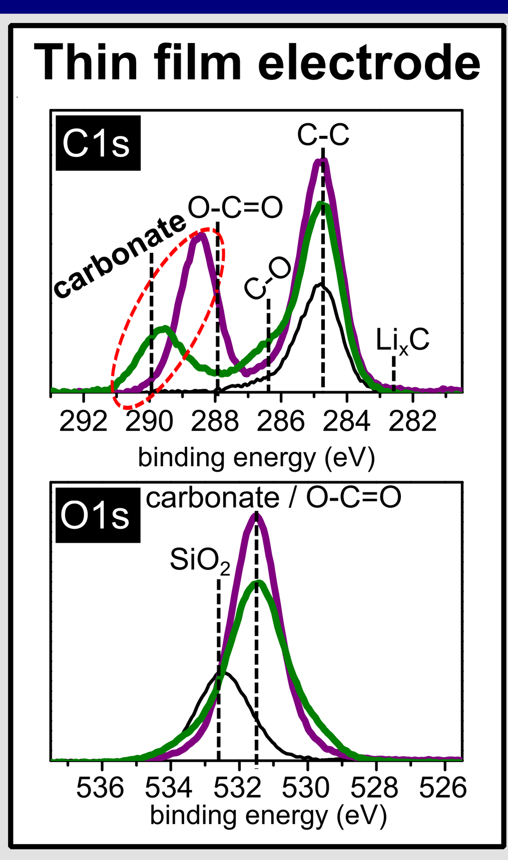


Fig. 7:
Results on thin film electrodes are comparable to those on composite electrodes. FEC additive leads to formation of carbonate species in the SEI. Differences in peak intensity ratios of thin films and composite electrodes in the C1s window occur due to binders and carbon additives.

SEI formed by FEC with high amounts of LiF and polycarbonates. Li-to-F ratio of 1.7 supports ring-opening mechanism as proposed by Chen *et al.* [2]. Therefore, reduction via VC intermediate step [3] less likely.
SEI formed by SA lacks carbonate species in comparison to FEC additive. However, reason for cell crash in SA containing composite electrodes not clear. Maybe due to side reactions with binder?

Conclusions

- Additives with good performance on Si thin films do not necessarily improve cycle life of composite electrodes (SA, TPFPB, VC)
- FEC is best candidate for composite electrodes in half cells, but suffers from continuous FEC consumption, leading to additive depletion followed by quick capacity fade
- Continuous FEC consumption is even a bigger issue in full cells with a limited Li source
- FEC decomposition leads to the formation of LiF and polycarbonate species most likely via a ring-opening mechanism
- Comparing SA and FEC additive it appears that polycarbonates are mandatory for good performance of composite electrodes, but not for thin films

Further discussion

- Reason for capacity loss within first 20 cycles (Fig. 3/4)?
- What is the reason for capacity recovery at cycle 40, when using VC (Fig. 3)?
- When using FEC in composite electrodes, the bumps in Fig. 4 most likely indicate FEC depletion.What is the reason for the subsequent temporary recovery?

References

[1] S. Song and S. Baek, *Electrochem. Solid-State Lett.* **2**, A23 (2009)
[2] X. Chen, X. Li, D. Mei, J. Feng, M. Y. Hu, J. Hu, M. Engelhard, J. Zheng, W. Xu, J. Xiao, J. Liu, and J.-G. Zhang, *ChemSusChem* **7**, 549 (2014)
[3] V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching, and D. Aurbach, *Langmuir* **28**, 965 (2012)

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*results shown in Fig. 3/4 from master thesis P. Sutton

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