PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

Elucidating the surface reaction of a-Si thin film used as model electrode for Li-ion batteries

G. Ferraresi[1], L. Czornomaz[2], P. Novák[1], C. Villevieille[1], M. El Kazzi[1]

1 - Paul Scherrer Institut, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

2 - IBM Research-Zürich, Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland

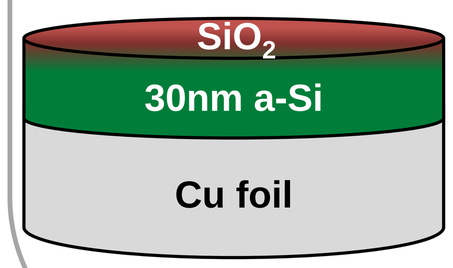
giulio.ferraresi@psi.ch

Motivation

Electrochemical and **surface analysis** (XPS) of 30nm amorphous n-type **Si thin films** (a-Si) **free of additives** (carbon, binder) as model electrode

Open questions:

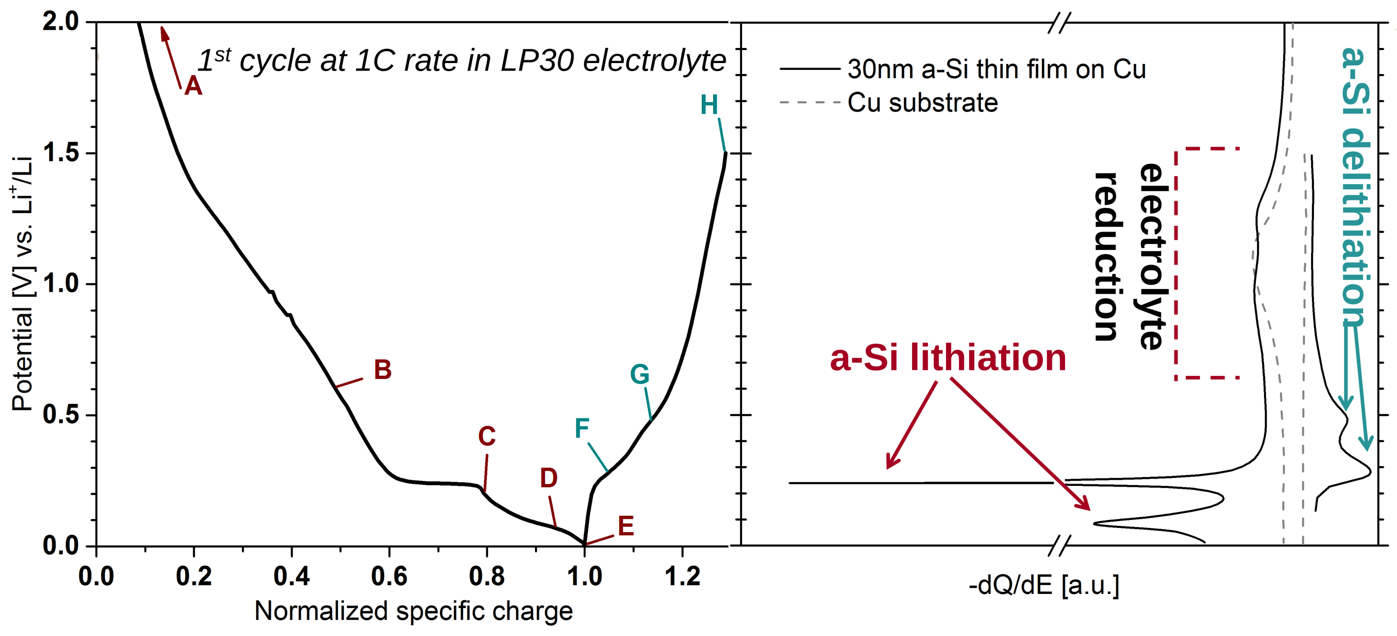
- Partial Si lithiation + Li-silicate irreversibility
- Reduction potentials of LP30 on a-Si thin film
- SEI composition and stability during 1st cycle

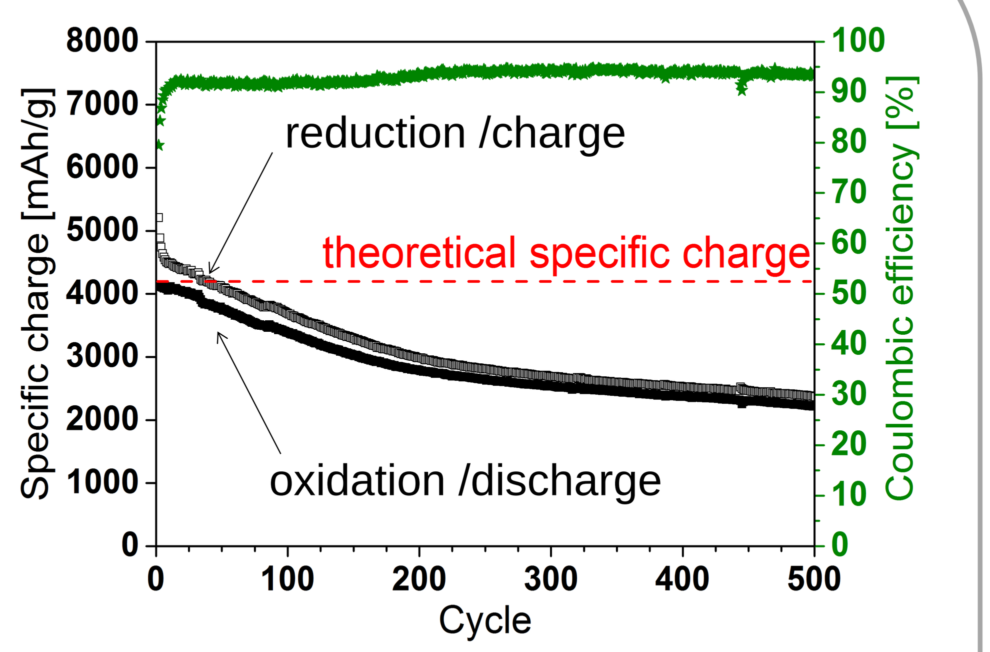


Model material:
30nm phosphorous-doped a-Si thin film on Cu foil
Technique: PECVD deposition

No binder, no conductive agent

Galvanostatic cycles

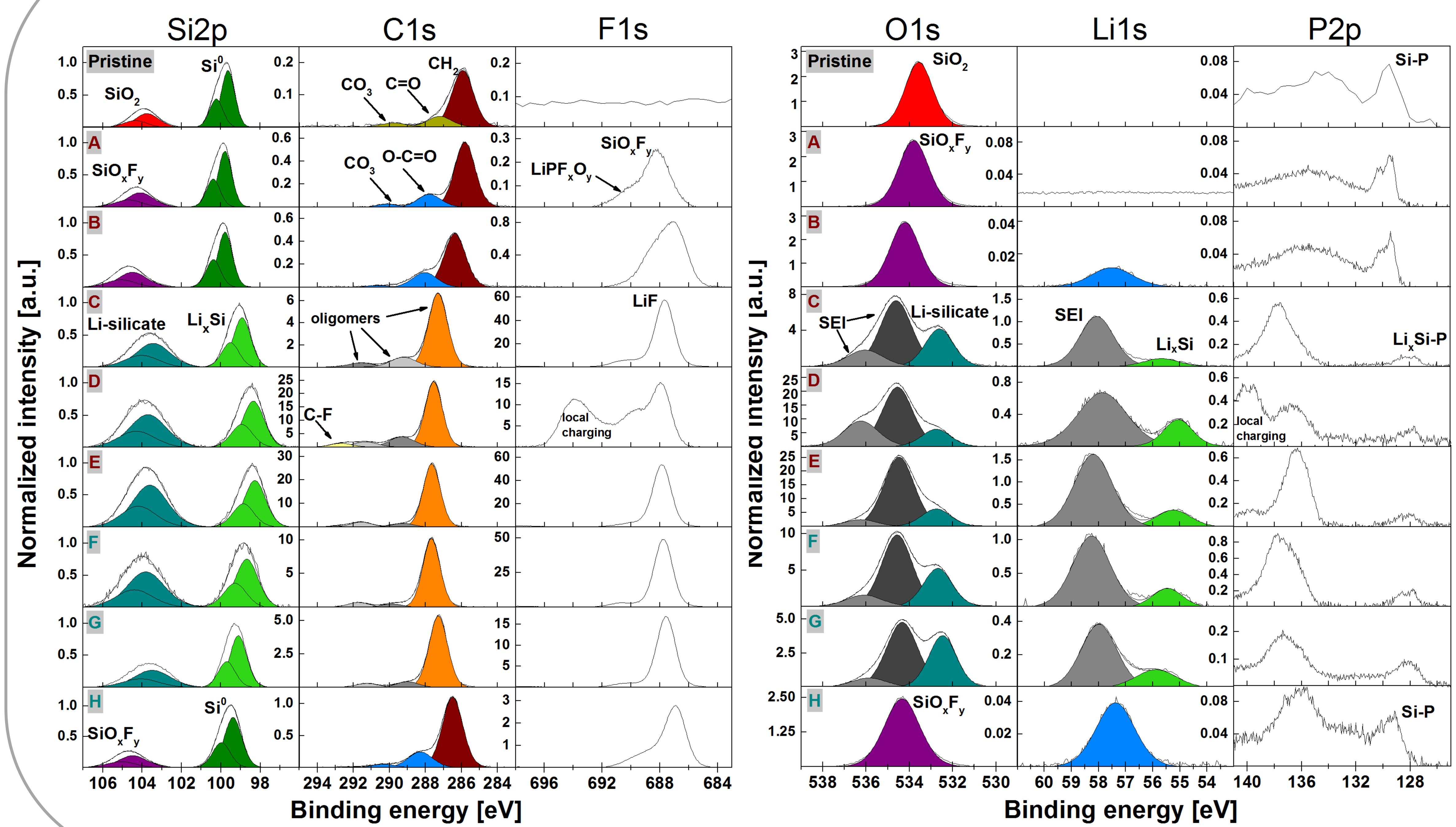


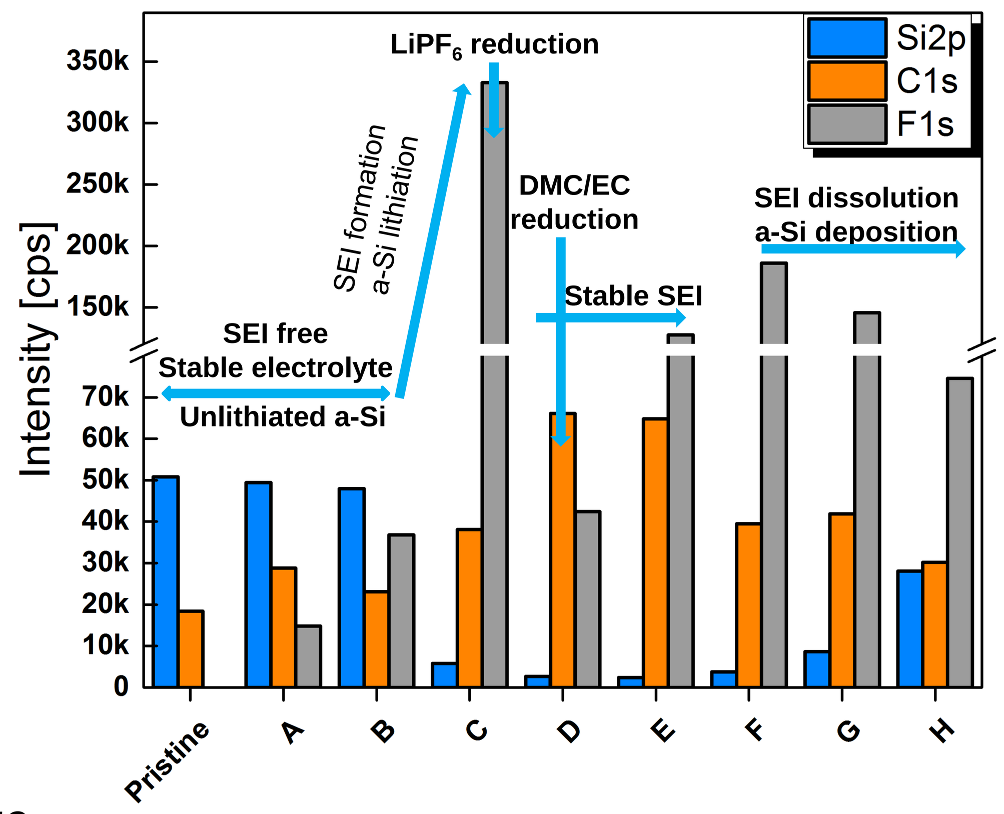


Selected potentials for post mortem XPS analysis								
Potential (vs. Li⁺/Li)	OCP	0.6 V	0.2 V	0.07 V	5 mV	0.28 V	0.47 V	1.5 V
Samples	A	B	C	D	E	F	G	H

- Elevated irreversible charge consumption (electrolyte decomposition)
- 50% initial specific charge after 500 cycles

Post mortem XPS investigation





Charge

A-B → No SEI formation, no electrochemical reaction involving a-Si film

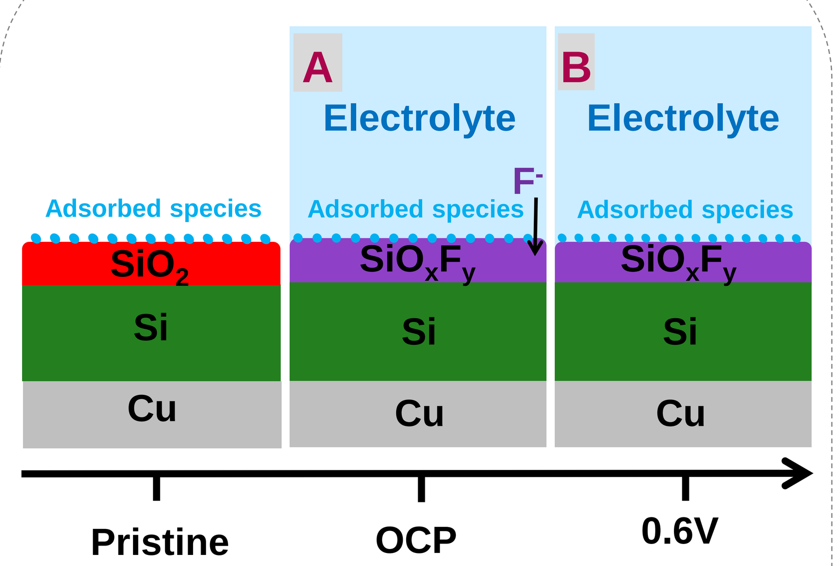
C-D-E → Li-silicate and Li_xSi alloy reactions, voltage-dependent SEI growth (at 0.2 V LiF clusters; at 0.07 V oligomeric matrix)

Discharge

F-G-H → Li_xSi and Li-silicate delithiation, SEI dissolution, partial loss of native oxide layer

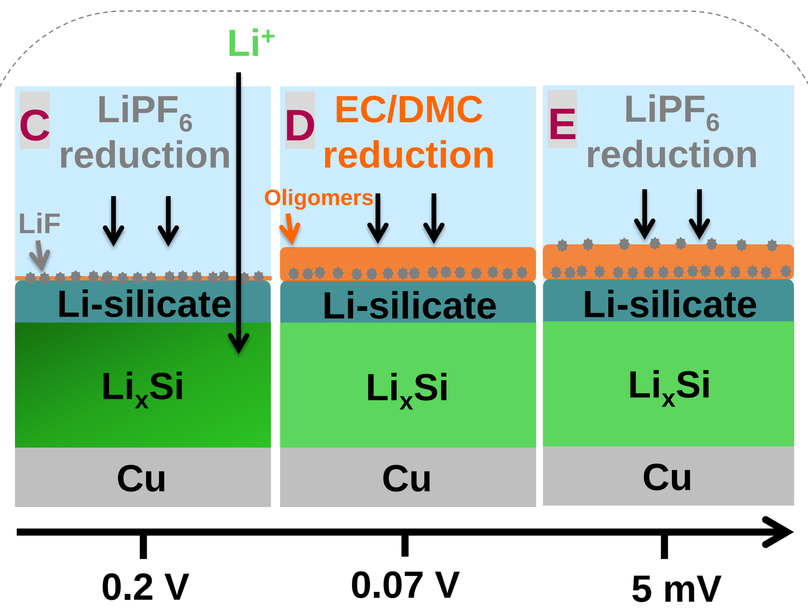
Reaction mechanism

Unlithiated a-Si – No SEI



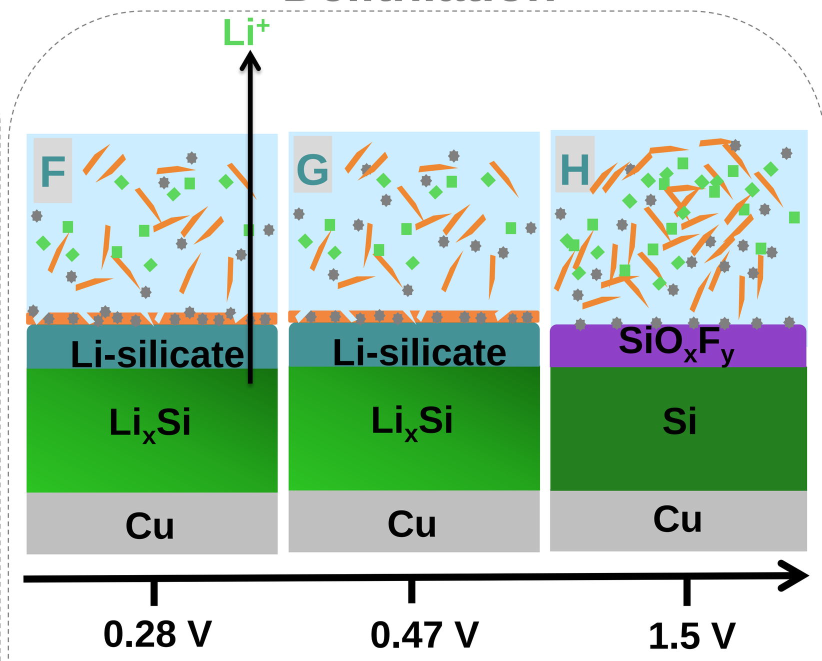
- **Adsorbed species** are **oxidised** in contact with LP30 electrolyte
  F^- (from $LiPF_6$) diffuses inside SiO_2 forming SiO_xF_y
- **No SEI** formation at **0.6 V** is detected

Lithiation



- xLi + Si → Li_xSi multi-step reaction
- **Li-silicate** formation
- Voltage-dependent SEI formation:
  0.2V -> LiF ($LiPF_6$ reduction)
  0.07V->oligomers (EC/DMC reduction)
  5mV -> mainly LiF clusters ($LiPF_6$)

Delithiation



- **Reversible** delithiation of Li_xSi and SiO_xF_y
- Li-silicate thickness is reduced
- **SEI decomposition** and **dissolution**

Conclusions/Outlook

- In-house XPS on **Si2p, C1s, Li1s, O1s, F1s and P2p core levels** to monitor SEI and Li-Si alloy reactions
- **No SEI** at voltage higher than **0.6V** during charge
- Voltage-dependent SEI formation: at **0.2V $LiPF_6$ is formed,** at **0.07V oligomers** form from EC/DMC reduction
- SiO_xF_y lithiation is reversible at the end of delithiation
- Model reaction mechanism to elucidate the **SEI growth mechanism** and **Li-Si alloy formation**
- XPS on long-term cycling will shed the light on SEI stability and Li_xSi alloy reversibility

Acknowledgements:
Financial support from the Competence Center Energy and Mobility (CCEM) and the Swisselectric research initiative is gratefully acknowledged