Surface investigation of 30nm amorphous Si thin films cycled as negative electrode for Li-ion batteries

G. Ferraresi¹, L. Czornomaz², P. Novák¹, C. Villevieille¹, M. El Kazzi¹

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 phosphorus doped (n-type) Si thin films (used as model material)
- Understand the properties of the solid electrolyte interphase (SEI) growth and Li-Si alloy formation upon lithiation/delithiation

**Electrochemical performances**
- Model material: 30nm P-doped Si thin film on Cu (PECVD deposition)
- No binder, no conductive agent

**Surface evolution**

**Post mortem XPS investigation**

**Post mortem XPS investigation**

**Conclusions**
- High stability of Si thin films during cycling
- Specific charge retention up to 50% of the initial value after 500 cycles
- In-house XPS on Si 2p, C 1s, Li 1s and O 1s core levels to monitor SEI and Li-Si alloy
- SEI forms only at potential lower than 0.6V
- Elucidation of the SEI growth mechanism and Li-Si alloy formation during the early stages of cycling

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**SEI and SiO₂ evolution**
- Breathing effect of the SEI
- SiO₂ thickness reduced after the first discharge

**Reaction mechanism**
- Li²⁺ and SiO₂ → Li-Si and Li-silicate compounds
- SEI (organic/inorganic) formation at potential lower than 0.6V

**Surface**

**Charge**
- Charge A → No SEI formation, no reaction involving silicon
- Charge B-D → SEI growth, Li-silicate and Li-Si alloy formation

**Discharge**
- Discharge E-G → Reversible Li-Si de-alloying, SEI removal, partial Li-silicate dissolution

**Charge**
- Charge E → Li-Si delithiated to Si²⁺
- Irreversible lithiation mechanism for SiO₂
- Li-silicate thickness is reduced
- SEI decomposition and dissolution

**Discharge**
- Discharge F → Li extraction
- Li₂SiO₂

**Li-Si reaction**
- SiO₂ → Si²⁺
- Li²⁺ and SiO₂ → Li-Si and Li-silicate compounds
- SEI (organic/inorganic) formation at potential lower than 0.6V