Role of the $LiPF_6$ Salt for the Long-Term Stability of Silicon Electrodes in Li-Ion Batteries - A Photoelectron Spectroscopy Study

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Objectives

- Understanding the interfacial chemistry taking place during charge/discharge since it partly explains the capacity fading of silicon observed upon cycling.
- Reaction of surface oxide, Li−Si alloying process, and passivation layer formation) has been investigated by photoelectron spectroscopy (XPS or PES).
- Both soft X-rays (hν=100−800 eV) and hard X-rays (hν=2000−7000 eV) from two different synchrotron facilities were used. The results are compared with those obtained with an in-house spectrometer (hν=1486.6 eV).

Why Silicon Anodes?

- Silicon can accommodate 3.75 Li atoms per Si atom at room temperature, resulting in a maximum capacity of 3579 mAh/g (8340 mAh/cm^3) which can be compared to the theoretical capacity of graphite, 372 mAh/g (818 mA/cm^3).
- Silicon is a light, abundant, and cheap material (the second most abundant element in the earth's crust after oxygen).

Challenges & Drawbacks

- Large volume expansion during alloying with Li will result in:

1. Strong mechanical degradation of the electrode;
2. Loss of electrical contact between silicon, carbon black and current collector;
3. Low Coulombic efficiency;
4. Decrease in capacity.

Solutions

- Reducing the size of the particles (nanostructured Si materials such as nanotubes, nanowires, or even more complex structures).
- New binders like carboxymethylcellulose sodium salt (CMC), poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), or natural polysaccharide alginate.
- Encapsulation of silicon within a rigid outer shell impermeable to electrolyte solvent molecules but permeable to Li ions.

Electrochemical Cycling

- Silicon electrodes: mixture of 80% (wt%) of crystalline silicon powder (∼50 nm, 70−100 m2/g, Alfa Aesar), 12% of the conductive additive carbon black (SuperP, Erachem Comilog), and 8% binder of sodium carboxymethyl cellulose (CMC, Mw = 700.000, DS = 0.9, Sigma Aldrich).
- A water−ethanol solution (EtOH/H_2O, 70/30) was used as solvent for the slurry preparation. The slurry was mixed in a Retsch planetary mill for 60 min and deposited on a 20 μm thick copper foil. It was then dried at 60 °C for 12 h in an oven, and the obtained coating had a thickness of ∼12−13 μm. Circular electrodes (2 cm diameter) were punched out and dried for 8 h at 120 °C in a vacuum furnace inside the argon glovebox (O_2<3 ppm, H_2O<1 ppm). The mass loading of the electrodes was 0.5 mg of Si per cm^2.
- Electrolyte: $LiPF_6$ at 1 mol/L dissolved in EC:DEC with ratio of 2:1.
- Cycling voltage window of 0.12-0.9 V with a current of 700 mA/g of silicon (≈C/5 with C the maximum theoretical capacity 3578 mAh/g).
- Before each PES characterization, the silicon electrode was carefully separated from the rest of the battery components in an argon glovebox and washed with dimethyl carbonate (DMC) solvent in three successive baths to remove the electrolyte.

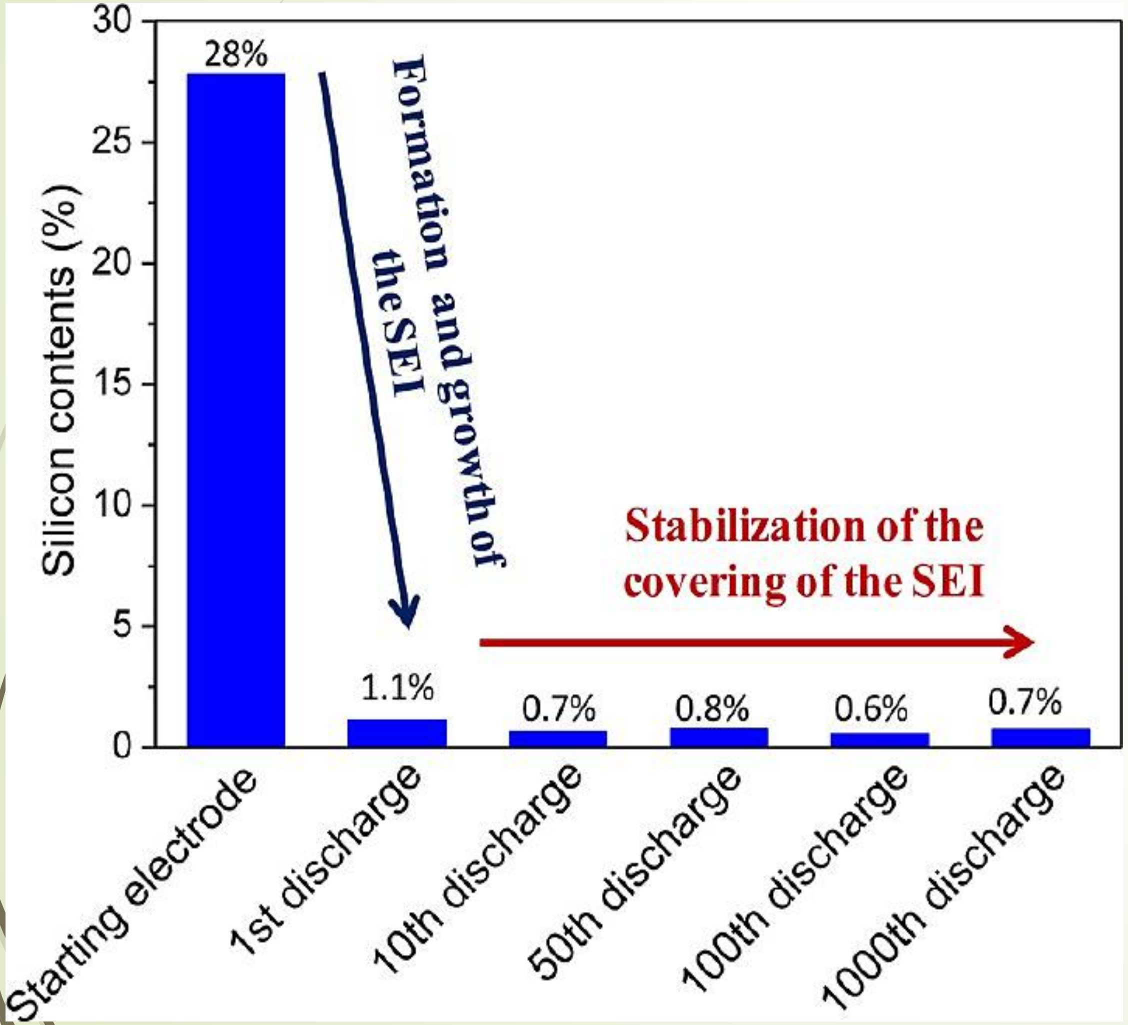
Soft X-ray PES measurements

- Max IV Laboratory synchrotron facility (I-411 beamline, National Synchrotron Radiation Laboratory, Lund, Sweden)
- Usable photon energies range from 50 to 1500 eV.
- The photoelectron kinetic energies (K.E.) were measured using a Scienta R4000 WAL analyzer.
- Two depths were investigated corresponding to a K.E of 130 and 590 eV.
- No charge neutralizer was used during the measurements.
- The pressure in the analysis chamber was about 10^{-8} mbar.

Hard X-ray PES measurements

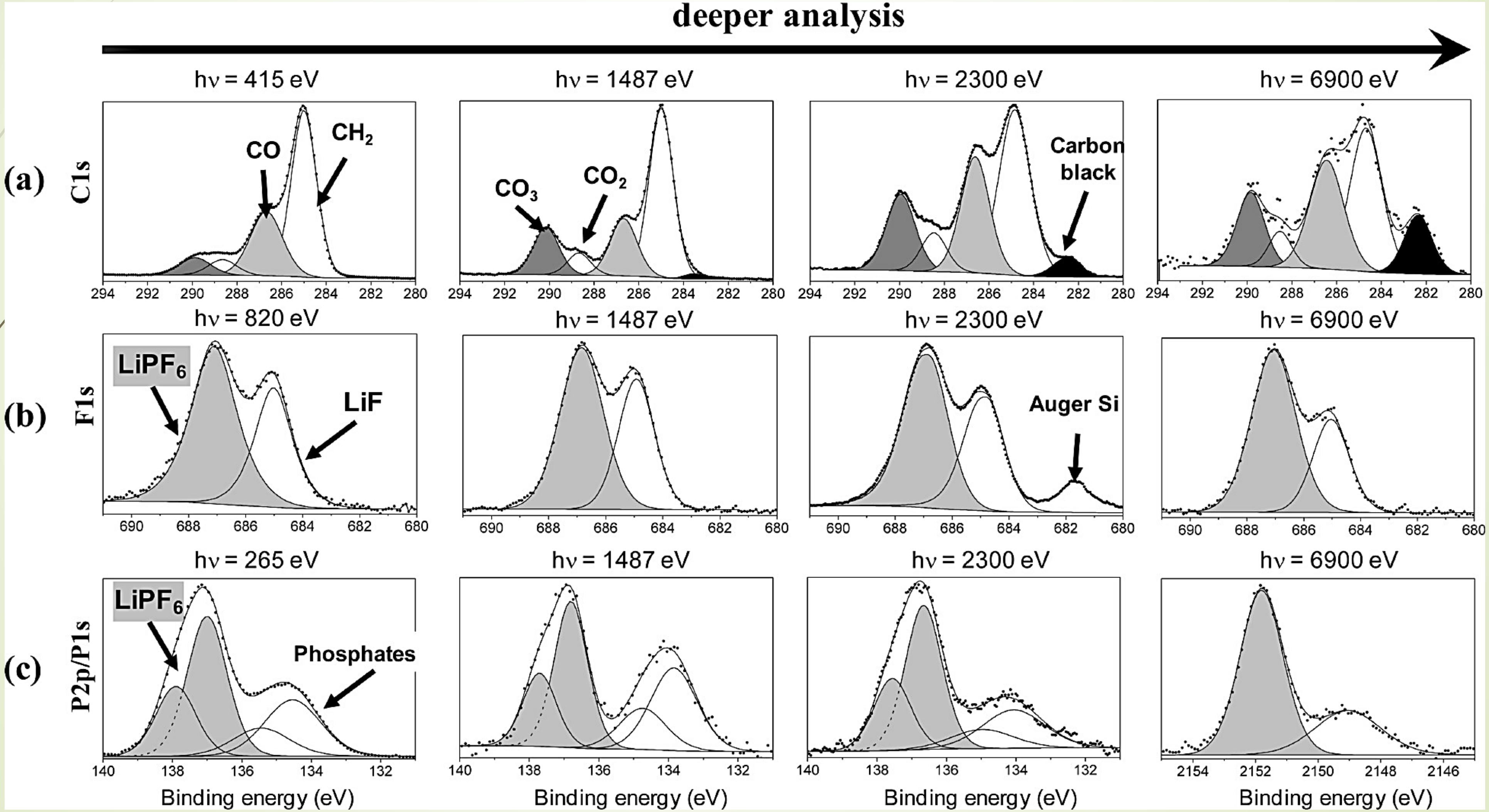
- BESSY II synchrotron facility (HIKE end station,31 KMC-1 beamline,32 Helmholtz Zentrum Berlin, Germany).
- Usable photon energies range from 2000 to 10000 eV.
- Fixed excitation energies were used, 2300 and 6900 eV (first order lights from respectively the Si(111) and the Si(422) double-crystal monochromator).
- The analyzer was a Scienta R4000 optimized for high kinetic energies up to 10 keV.
- No charge neutralizer was used.
- The pressure was around 10^{-8} mbar in the analysis chamber.

SEI Analysis during Long Cycling

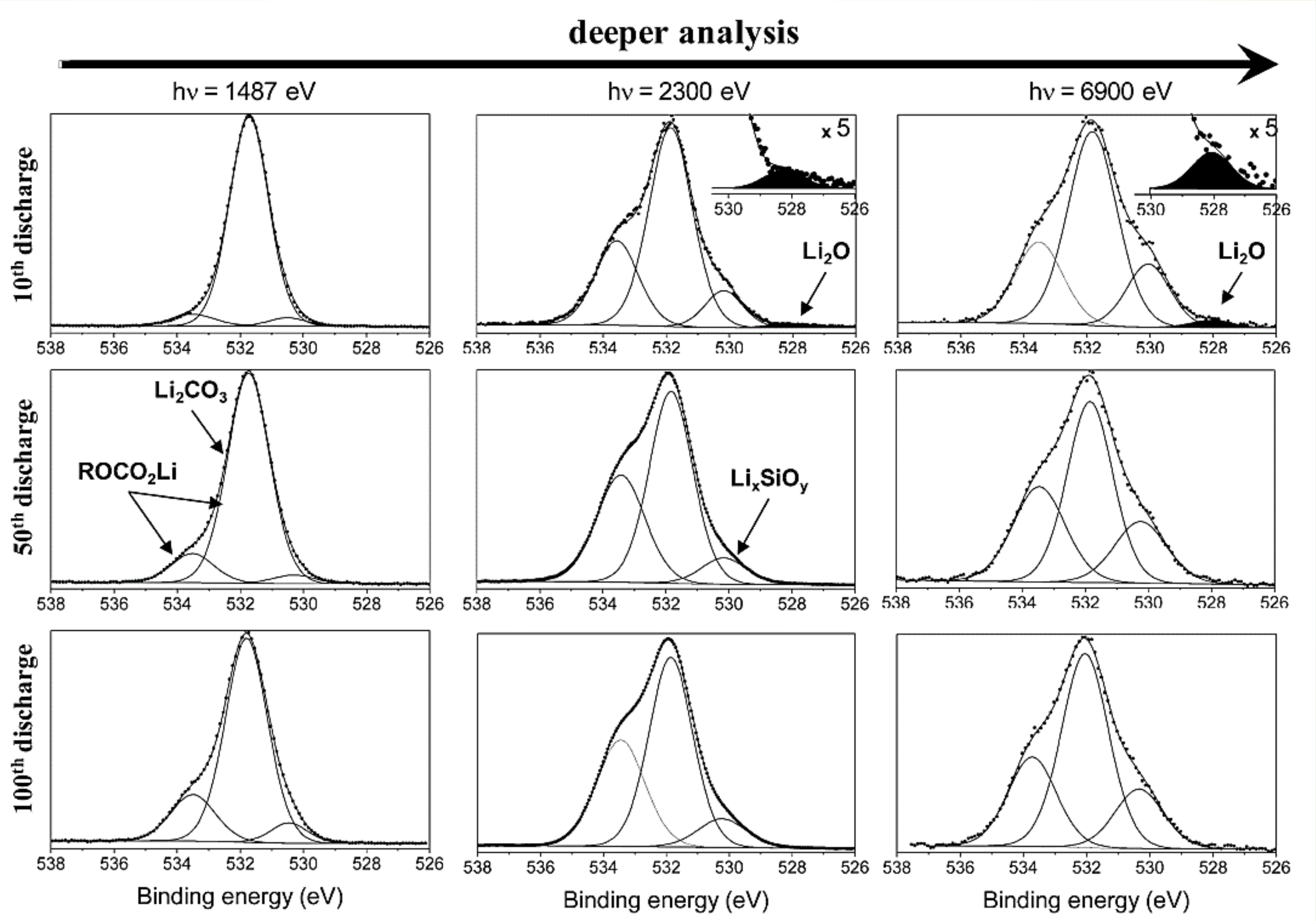


- The variations in atomic percentages reported in this histogram are an indirect measurement of the SEI thickness at the different cycles.
- All the phases containing silicon are found to be below the SEI layer containing all the other elements present in our system (C, O, F, P, and Li), so silicon atomic percentages appear as a good indicator for the variation of the SEI thickness.
- Dramatic drop of the Si 2p signal between the starting electrode (28%) and the 1st discharge following the precycling step (1.1%). After the 10th discharge, the atomic % has decreased to 0.7%.
- After the 10th cycle, and all the way up to the 1000th discharge, the atomic % stays around 0.6–0.8% showing that the SEI covering of the silicon particles is quite stable during continuous cycling.

SEI Composition



O 1s Spectra


deeper analysis
hν = 1487 eV
hν = 2300 eV
hν = 6900 eV
10th discharge
50th discharge
100th discharge
x 5
Li$_2$O
Li$_2$CO$_3$
ROCO$_2$Li
Li$_x$SiO$_y$
538 536 534 532 530 528 526
Binding energy (eV)

Discussion

- The four main components visible in these four spectra (in white and gray) represent the carbonaceous species deposited at the surface and among them the characteristic peaks corresponding to binding energy values for C−O (286.5 eV), O=C−O (288.5 eV), and CO_3 (290 eV) carbon environments.
- It can be seen that the ratio of CO_3/CO_2 and of CO_3/CO slightly increases as a function of the analysis depth and especially between hν = 410 and 1486.6 eV. This suggests that Li_2CO_3 is found preferably close to the active particle.
- In the C 1s spectra a fifth surface component appears at low binding energy (~282−283 eV) at the greatest analysis depth. This peak, assigned to carbon black, gradually increases with increasing photon energy. If we look at the atomic % of carbon black detected in the first 5−10 nm (in-house PES), we can see that the content is very stable (around 0.5%) after the 10th, 50th, and 100th discharges, respectively. The presence of this component confirms the thickness stability of the SEI upon cycling.

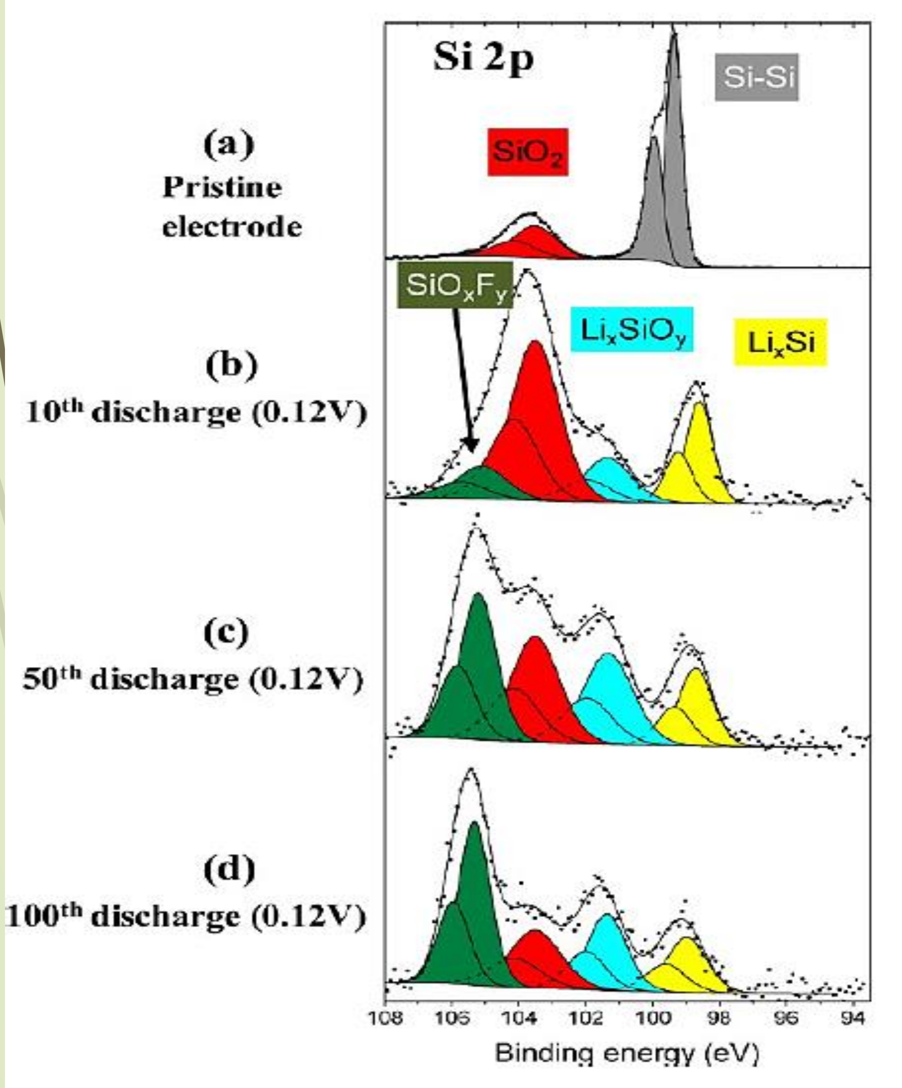
Discussion

- After the 1st discharge, various oxygenated species are formed on the particle surfaces and in the SEI layer. Their specific signatures are in a narrow binding energy range, so a precise interpretation of the O 1s spectra is complex. However, we can see that after 10, 50, and 100 cycles, the O 1s spectra are rather similar to the ones obtained after a single discharge. The component with the maximum intensity has a binding energy around 532 eV for all the analysis depths, and there is also a component at higher binding energy (∼533.5 eV). These two signatures are in good agreement with carbonates, alkyl carbonates, and other organic species commonly found in SEI with carbonates solvents. The component at ∼530−530.5 eV is attributed to the lithium silicate Li_4SiO_4.
- O1s peaks indicate that the SEI is homogeneous in composition and thickness during cycling, and this is especially demonstrated with the analysis of the data from the greatest analysis depths (2300 and 6900 eV) which means that the part of the SEI closest to the electrode materials is very stable. Small fluctuations are, however, visible at the lowest depths (hν = 1486 eV).

Discussion

- In the measurements with largest analysis depth performed after the 10th discharge, an additional barely visible peak with a low specific binding energy (at 528−528.5 eV) is detectable and can be assigned to Li_2O. In the charged state, no peak could be detected at this binding energy.
- Reaction of lithium with silicon oxide can occur for nano-sized particles and that this leads to the reduction of the surface oxide:
- $SiO_2 + 4Li \rightarrow Si + 2Li_2O$
- Li_2O was formed during the 1st discharge and that its formation was reversible upon the 1st cycle. The spectra allow us to say that the formation of Li_2O is reversible at least during the 10th 1st cycles but that the amount of Li_2O is decreasing upon cycling.
- After 50 and 100 discharges, Li_2O is not detected anymore in any of the O 1s spectra suggesting a consumption of this species.

Evolution of Si Compounds



- The irreversible formation of a lithium silicate compound: Li_4SiO_4, by reaction of the lithium with the silicon dioxide present at the surface of the Si nanoparticles. At the same time, the formation of the Li−Si alloy during the first lithium insertion process has been clearly illustrated.
- After the 50th and 100th discharge (c and d), the same four components are identified as after the 10th discharge. Upon cycling, we can clearly observe a significant increase of the amount of the fluorinated Si species even if the lithium silicate and the silicon oxide formed during the first lithiation are still present after 100 cycles.

Nature of the Fluorinated Phase

- The fluorinated phase formed at the extreme surface of the silicon nanoparticles is due to a process occurring between the particles and the only source of fluorine which is the electrolyte salt $LiPF_6$.
- $LiPF_6 \rightarrow LiF + PF_5$ $PF_5 + H_2O \rightarrow POF_3 + 2HF$
- In organic carbonate electrolytes the equilibrium of the process can be shifted to the right due to the interaction between PF_5 and solvent molecules.
- The liberation of protons during formation of LiF ($Li^+ + HF \rightarrow LiF + H^+$) can also increase the rate of the process by an autocatalytic mechanism. In the present case, the generated HF can react with the native oxide at the surface of the silicon electrode modifying the favorable interactions between the binder and the active material surface.
- Silica dissolution by HF is a surface reaction-controlled process with adsorption of HF and HF_2^-, this last species being nearly four to five times more reactive than HF. The catalytic actions of H^+ ions has also been pointed out especially for HF solutions of extremely low concentrations.
- The gradual disappearance of Li_2O during cycling previously observed can be put in parallel with the gradual appearance of the fluorinated silicon species. Li_2O can easily react with HF and form LiF. $Li_2O + HF \rightarrow LiF + H_2O$
- The formation of water allows the regeneration of HF.
- Both the consumption of Li_2O and the formation of the fluorinated species are enhanced during cycling.

Conclusions

- By the original use of depth-resolved PES based on the use of different X-ray photon energies on a Si/C/CMC composite electrode together with SEM investigations, we have demonstrated valuable information on the role of the LiPF6 salt for the chemistry of the silicon electrode during cycling. We have followed the chemistry occurring at the surface of Si nanoparticles in addition to its high influence on the SEI chemical composition. We have also illustrated the crucial importance of how the cycling procedure influences the overall surface morphology of the electrode. The adopted capacity limitation (cutoff potential of 0.12 V) results in the reduction of the amount of cracks formed in the electrode during lithium extraction. As a consequence, less electrolyte and lithium ions are lost by reconstruction and/or a constant growth of the SEI.
- When the SEI has been formed (mainly during the 1st discharge), its chemical composition and its covering properties are stable during the subsequent cycling of the electrode. The chemical composition seems to be quite homogeneous within the SEI layer especially considering the inorganic compounds (LiF, $LiPF_6$, phosphates). Some fluctuations at the extreme surface of the SEI are noticed for the organic part (oxygenated and carbonaceous components).
- In the analysis of the surface of the active particles, a fluorinated silicon species (SiO_xF_y, $y \leq 3$) appears during cycling at the interface between the Si particles and the SEI.
- Combining these observations and literature data, it is possible to explain the formation of such a phase pointing out the important role of HF resulting from $LiPF_6$ degradation. The Li_2O phase is present only in the lithiated state, and it slowly disappears upon cycling, which may also be an effect of HF.

Thanks for your attention.