

## Interfacial processes on single crystal Si electrodes in organic electrolytes

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Silicon is a promising anode material for commercial Li-ion batteries mainly due to its high specific capacity of 4200 mAh/g.[1] However, the key problems are a large volumetric change  $\sim 310\%$  during the lithiation/delithiation processes, poor intrinsic electronic conductivity of silicon, and interfacial instability of Si electrodes in organic electrolytes.[2] These effects contribute to a poor electrochemical performance and low coulombic charge/discharge efficiency, especially during the first few cycles. Electrolyte additives such as vinylene carbonate (VC), fluoroethylene carbonate (FEC) and/or the use of the CMC binder tends to improve the electrode cycle stability, and consequently battery lifetime and efficiency. [3,4,5,6,7,8]

This work presents fundamental studies of interfacial phenomena on single crystal Si electrodes in organic electrolytes in regards to their electrochemical behavior in Li ion batteries. Different Si crystal facets exhibit different electrochemical response upon polarization at potentials  $<2.5$  V vs. Li/Li<sup>+</sup>. Moreover, different crystal facets display notably distinct physico-chemical properties e.g., wettability with the electrolyte and strength of hydrogen-hydrogen interactions with the CMC binder. Figure 1 depicts the differences of the wettability with water depending on the silicon crystal orientation.

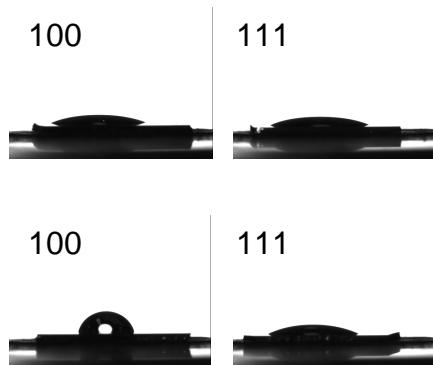


Figure 1. Contact angle dependency on the crystal orientation of silicon wafers (100) and (111) with 1M LiPF<sub>6</sub> EC:DEC [3:7] (top) and with water as sample liquid (bottom).

The solid electrolyte interphase (SEI) formation on the facets (100), (110) and (111) was controlled electrochemically during the first potentiostatic charge in a three electrode cell and the resulting surface layer was investigated by FTIR, LIBS and XPS spectroscopy. Remarkable quantitative and qualitative differences in the electrochemical spectroscopic response were observed,

depending on the surface crystal orientation of silicon. Chemical composition of the SEI layer varied strongly on the different crystal orientations at potential  $>0.5$  V of Si and included LiPF<sub>6</sub> salt and EC and DEC solvents decomposition products.

At potentials below 0.5 V the SEI undergoes reformation due to Si cracking and structural transition from crystalline to amorphous silicon upon alloying with lithium. Figure 2 displays the different FTIR spectra of the SEI at the (111) Si electrode at 0.5 and 0.01 V.

The correlation between surface activity, composition and stability of the SEI layer and crystal orientation will be presented and discussed.

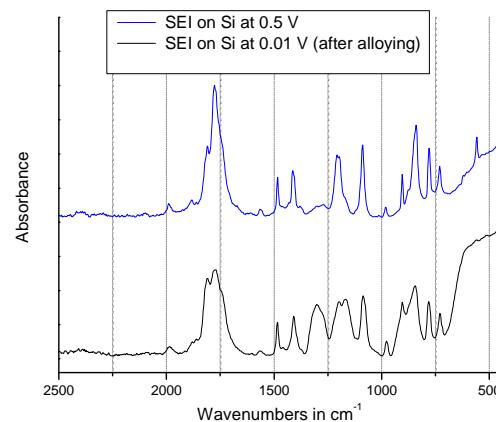


Figure 2. FTIR spectra of the SEI layer on the Si (111) electrode at 0.5 and 0.01 V, before and after alloying with lithium in 1M LiPF<sub>6</sub> EC:DEC [3:7]

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