In situ scanning tunneling microscopy studies of the SEI formation on graphite electrodes for Li(+)‐ion batteries

The SEI-formation on graphitic electrodes operated as an Li(+)‐ion battery anode in a standard 1 M LiPF6 EC/DMC (1:1) electrolyte has been studied in situ by EC-STM. Two different modes of in situ study were applied, one, which allowed to follow topographic and crystallographic changes (solvent cointercalation, graphite exfoliation, SEI precipitation on the HOPG basal plane) of the graphite electrode during SEI-formation, and the second, which gave an insight into the SEI precipitation on the HOPG basal plane in real time. From the in situ EC-STM studies, not only conclusions about the SEI-topography could be drawn, but also about the formation mechanism and the chemical composition, which strongly depend on the electrode potential. It was shown that above 1.0 V vs. Li/Li(+) the SEI-formation is still reversible, since the molecular structure of the solvent molecules remains intact during an initial reduction step. During further reduction, the molecular structures of the solvents are destructed, which causes the irreversible charge loss. The STM studies were completed by electrochemical methods, like cyclic voltammetry, the potentiostatic intermittent titration technique and charge/discharge tests of MCMB electrodes.