

### Monitoring Electrolyte Reduction Mechanisms by Advanced Electrochemical in situ Methods

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#### Introduction

Although SEI (=solid electrolyte interphase) formation mechanisms are one of the most widely studied phenomena in the field of lithium ion batteries, they are not fully understood yet. Especially the failure mechanism of graphite electrodes in propylene carbonate (PC) based electrolytes is still under controversial debate [1,2].

This contribution reports on the application of advanced electrochemical in situ methods (electrochemical dilatometry, online mass spectrometry and in situ X-ray diffraction) that allow to monitor changes of the active material (e. g. volume changes, structural changes) or changes at the electrode / electrolyte interface (e.g., gas formation) in parallel to the electrochemical experiment. Specially designed electrochemical cells and electrodes, as described elsewhere, have been used for the dilatometric, online MS and in situ X-ray investigations [2,3].

#### Results

At fast scan rates, e. g. 10 mV/s, graphite electrodes react reversibly in PC based electrolytes. Fig. 1 shows a cyclic voltammogram and the corresponding dilatation record of a TIMREX T200-2000 graphite sample in 1M LiClO<sub>4</sub> / PC electrolyte. The dilatometric plot reveals that "breathing" of the electrode occurs. The extent of the overall relative volume expansion of the graphite sample (d / %) observed by dilatometry is far too much for the intercalation of unsolvated lithium cations. The most reasonable explanation is the intercalation of PC-solvated lithium cations. This data is strongly supported by in situ X-ray analyses where the formation of ternary solvated graphite intercalation compounds in PC based electrolytes has been monitored (Fig. 2) [3]. As the formed intercalates are kinetically unstable, decomposition reactions under the release of gaseous products occur within the graphite structure. Propylene gas as the major gaseous reduction product of propylene carbonate was measured by online mass spectrometry (Fig. 3).

#### Conclusion

The presented data gives strong evidence that the electrolyte reduction mechanisms in PC proceeds via the decomposition of ternary solvated intercalation compounds (Li<sup>+</sup>(PC)<sub>y</sub>C<sub>n</sub><sup>-</sup>). As a consequence, gas evolution takes place inside the graphite and the formed gas could act as strong lever enabling exfoliation and mechanical destruction of graphite.

#### Acknowledgements

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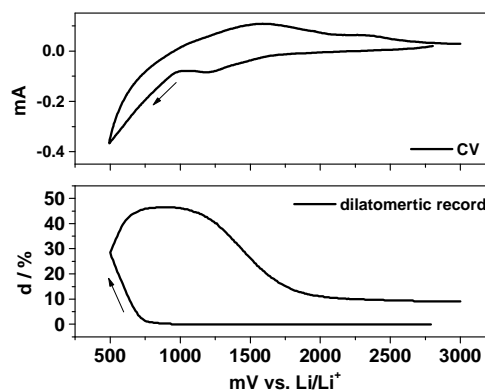


Fig. 1: CV (top) and dilatation record (bottom) of a TIMREX T200-2000 graphite sample in 1M LiClO<sub>4</sub> / PC electrolyte. Scan rate 10 mV / s, reverse potential = 500 mV.

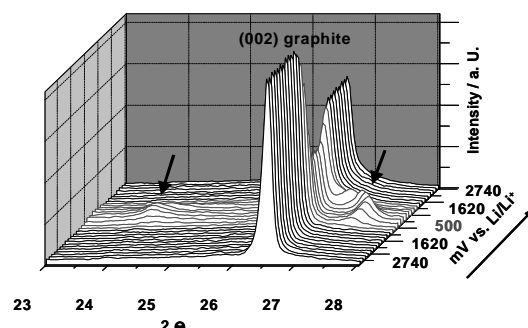


Fig. 2: In situ X-ray data (Cu K<sub>α</sub>) of a SFG 44 graphite electrode during a cyclic voltammogram (reverse potential = 500 mV, scan rate 10 mV/s) scan. X-ray evidence for the formation of a ternary solvated graphite intercalations compound is marked by arrows.

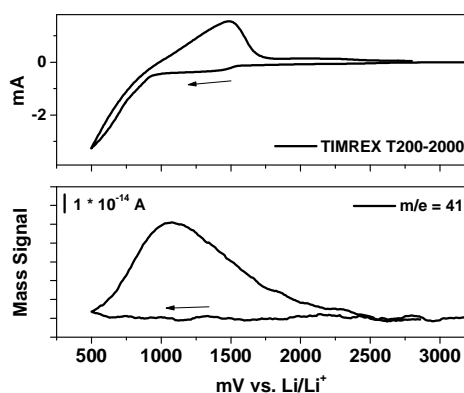


Fig. 3: CV (top) of a TIMREX T200-2000 graphite electrode in 1M LiClO<sub>4</sub> / PC electrolyte. Scan rate 10 mV/s, reverse potential = 500 mV. Mass spectrometric cyclic voltammogram (MSCV, bottom) represents propylene gas evolution (m/e = 41).

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