

# Solvent co-intercalation, gas evolution, and SEI formation at anodes in cyclic carbonate (PC, EC) based electrolytes

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## Introduction

The most important prerequisite for good electrode functioning in Li-ion batteries was found to be a passivating surface layer that derives from electrolyte decomposition products (SEI). Therefore, investigations concerning SEI formation mechanisms are a key issue in the field of Li-ion battery technology [1, 2]. This contributions reports on solvent co-intercalation reactions at graphite electrodes that have been monitored in ethylene carbonate (EC) and propylene carbonate (PC) based electrolytes by advanced electrochemical in situ methods. Special emphasis is laid on the connection between solvent co-intercalation reactions and the evolution of gaseous electrolyte decomposition products.

## Results

As an example figs. 1, 2 represent online mass spectrometry experiments with graphite electrodes in 2M LiClO<sub>4</sub> / EC electrolyte that were performed as follows: Following a fast potention-dynamic step with 10 mV/s from ca. 3.0 to 0.5 V vs. Li/Li<sup>+</sup>, the electrode has immediately been kept at open circuit. At open circuit, the electrode potential and the mass signal of ethylene gas have been recorded vs. time. At the fast scan rate of 10 mV/s only small areas of the graphite react, only small, but still significant gas evolution can be recorded: During the voltammetric scan the reduction reaction below 1 V vs. Li/Li<sup>+</sup> is followed by ethylene gas evolution (MSCV, Fig. 1). At open circuit the electrode potential jumps from 0.5 V to ~ 0.75 V vs. Li/Li<sup>+</sup>, where a potential plateau develops (Fig. 2). This plateau potential is typical for solvated graphite intercalation compounds (sGICs) and is also observed for propylene carbonate electrolytes, however, at higher potentials > 1V in the latter case [3]. The formed sGICs are only kinetically stable and gradually decompose during time, which is visible by a gradual change of the measured parameters: (i) The open circuit potential shifts to more positive values and (ii) ethylene gas evolves, the gas being most likely a decomposition product of the solvated intercalates (fig. 2). Fig. 3 compares the electrode potentials at open circuit following a fast potention-dynamic step with 10 mV/s from ca. 3.0 to either 0.65, 0.5 and 0.4 V vs. Li/Li<sup>+</sup> in 2M LiClO<sub>4</sub> / EC electrolyte. It is observed that the length of the plateau potentials at open circuit is dependend on the end potential of the potention-dynamic step and thus, on the amount of solvent co-intercalation.

## Conclusion

The experiments indicate that solvent co-intercalation reactions occur in EC and PC based electrolytes. As each intercalated solvent molecule has individual contact to the intercalated lithium and the electronically conducting graphite matrix, a self-decomposition of the intercalate

species can be expected. However, EC and PC sGICs seem to be different in terms of their kinetic stability vs. reduction.

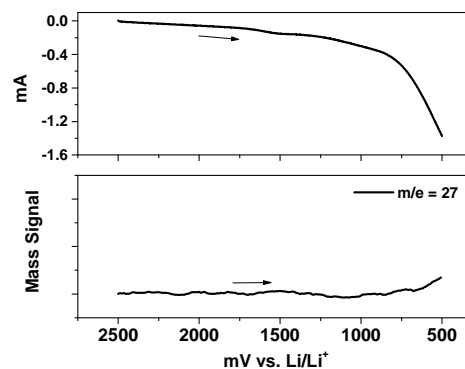


Fig. 1: Linear cathodic scan and corresponding mass spectrometric cyclic voltammogram (MSCV). Scan rate: 10 mV/s, end potential = 500 mV.  $m/e = 27$  indicates ethylene formation. TIMREX T200-2000 graphite, 2M LiClO<sub>4</sub> / EC electrolyte.

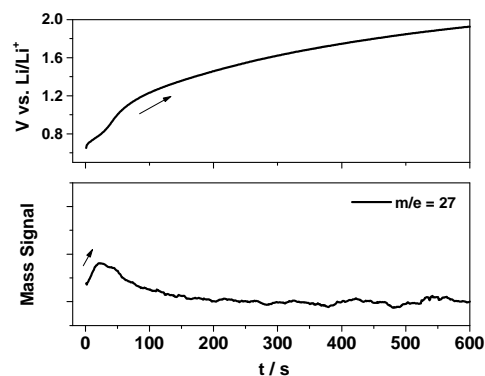


Fig. 2: Open circuit potential and corresponding ethylene gas evolution ( $m/e = 27$ ) vs. time. TIMREX T200-2000 graphite, 2M LiClO<sub>4</sub> / EC electrolyte.

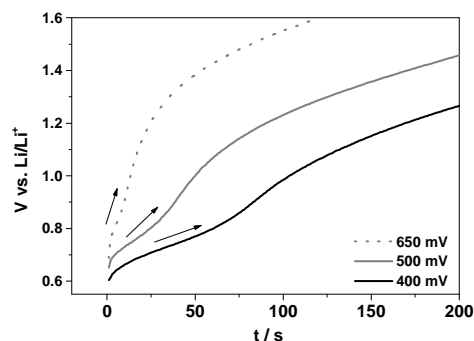


Fig. 3: Comparison of open circuit potentials vs. time following a fast potention-dynamic charging step with 10 mV/s from ca. 3.0 to either 0.65, 0.5 and 0.4 V. TIMREX T200-2000 graphite, 2M LiClO<sub>4</sub> / EC electrolyte.

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