PROPYLENE GAS EVOLUTION IN PC BASED ELECTROLYTE AND THE CONNECTION TO PC CO-INTERCALATION INTO GRAPHITIC ANODES

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Introduction

Crystalline graphites usually can not be operated in propylene carbonate (PC) electrolytes, unless effective film forming electrolyte additives are used [1]. Manifold problems are associated with the combination of PC with graphite, including: propylene gas evolution [2], creation of solvated graphite intercalation compounds (sGICs) [3], and graphite exfoliation. Recently, we [4] found that propylene evolution can only be observed at graphite, but not with metallic anodes, either lithium non-active, e.g., Cu and Ni, or lithium-active, e.g., Li, Sn, and SnSb.

Experimental

In order to monitor gas evolution and graphite expansion in parallel to the electrochemical experiment we took use of on-line mass spectrometry and *in situ* dilatometry. For both setups, the experiments were performed as follows: Following a fast potentio-dynamic step with 10 mV.s⁻¹ from ca. 3.0 to 0.5 V vs. Li/Li⁺, the electrode has immediately been kept at open circuit. At open circuit, the potential, the mass signal of propylene (MS), and the relative expansion/contraction have been recorded vs. time.

Results and Discussion

At these fast scan rates only small areas of the graphite react, only small, but still significant expansions/ contractions and mass signals can be recorded: During the voltammetric scan the intercalation /reduction reaction at ca. 1 V vs. Li/Li⁺ is followed by graphite expansion (Fig. 1). At open circuit the graphite potential jumps from 0.5 V to >1 V vs. Li/Li⁺ (Fig. 3a, 4a) because the formed sGICs are only kinetically stable and decompose, which is visible by the change of the measured parameters: (i) Propylene gas evolves, the gas being a decomposition product of the solvated intercalates (Fig. 4b), and (ii) the expanded graphite matrix shrinks (Fig. 3b). When the potential becomes more positive gas evolution appears to stop and deintercalation of solvated Li⁺ seems to be the major reaction being responsible for the shift to more positive values (Figs. 3, 4). In summary, the compared to other anode materials unique propylene gas evolution process

at graphite, can be explained by decomposition of sGICs, as only graphite is vulnerable to solvent co-intercalation. Apparently, the decomposition products of the sGICs, which are created apart from propylene, do not form an effective SEI hindering further co-intercalation. Thus, even when only a limited graphite area may be subject to solvent co-intercalation (which may be not visible by XRD), gas evolution takes place inside graphite and the formed gas could act as strong lever enabling exfoliation and mechanical destruction of graphite.



Fig. 1 CV (a) rel. dilatation (b) of graphite TIMREX T200-2000 in 1 M LiClO₄ in PC. Scan rate: 10 mV.s^{-1} .



Fig. 2: CV (a) and MSCV (b) of graphite TIMREX T200-2000 in 1 M LiClO₄ in PC. The mass signal m/e = 41 represents propylene. Scan rate: 10 mV.s⁻¹.



Fig. 3: Potential (a) and rel. dilatation (b) recorded vs. time of graphite TIMREX T200-2000 in 1 M LiClO₄/PC.



Fig. 4: Potential (a) and mass signal (b) recorded vs. time of graphite TIMREX T200-2000 in 1 M $LiCIO_4$ in PC The mass signal m/e = 41 represents propylene.

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