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Gas evolution in activated carbon/propylene carbonate based double-layer capacitors

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Abstract

For the first time gas evolution in a double-layer capacitor cell employing activated carbon electrodes and a solution of 1 M $(C_2H_5)_4NBF_4$ in propylene carbonate (PC) has been monitored by means of on-line mass spectrometry (DEMS). During slow scan voltammetry, CO_2, propene, and H_2 were detected as the major gaseous decomposition products. Probably propene and H_2 are formed by solvent reduction at the negative electrode, while CO_2 is formed by solvent oxidation at the positive electrode. A small amount of propene is already detected at a cell voltage of below 1 V. For all species the onset of significant gas evolution coincides roughly with the rise of faradaic currents. The increase of coulombic efficiency during subsequent cycling is attributed to passivation processes taking place at both electrodes.

Keywords: On-line mass spectrometry; Head space analysis; Electrochemical double layer capacitor; Activated carbon; Propylene carbonate decomposition

1. Introduction

In order to guarantee the extra-ordinary life time and cycle stability of today's electrochemical double layer capacitors (EDLC) their maximum cell voltage has to be limited to below 2.7 V [1]. Especially in terms of energy density this limitation is a serious drawback of EDLCs compared to, e.g., secondary lithium-ion batteries with cell voltages above 4.0 V. One focus of current research is therefore to understand the processes limiting the EDLC operation voltage.

Only recently, we have shown that intercalation processes and the simultaneous dimensional changes can limit the accessible EDLC voltage range [2]. In the present work a more obvious cause of ageing and failure is addressed, namely the formation of gaseous products upon electrolysis of the electrolyte solution.

In the past, the electrochemical stability of propylene carbonate (PC) containing electrolytes has extensively been studied in the context of lithium-ion batteries, both with metallic lithium and with carbon based negative electrodes. Recently, the subject has been reviewed by Xu [3]. The stability of PC against lithium has been attributed to the formation of a protective layer, the so-called solid electrolyte interphase (SEI) [4]. Later on, this model was also adapted to the case of carbonaceous electrodes. The SEI is believed to consist mainly of Li_2CO_3 and oligomeric/polymeric alkyl carbonates which are formed via the radical anion shown in Scheme 1 (adopted from Table 6 in [3]). This intermediate may, e.g., dimerise and release propene. In agreement with this mechanism, propene is found as the main gaseous reduction product upon SEI formation in PC based electrolytes.

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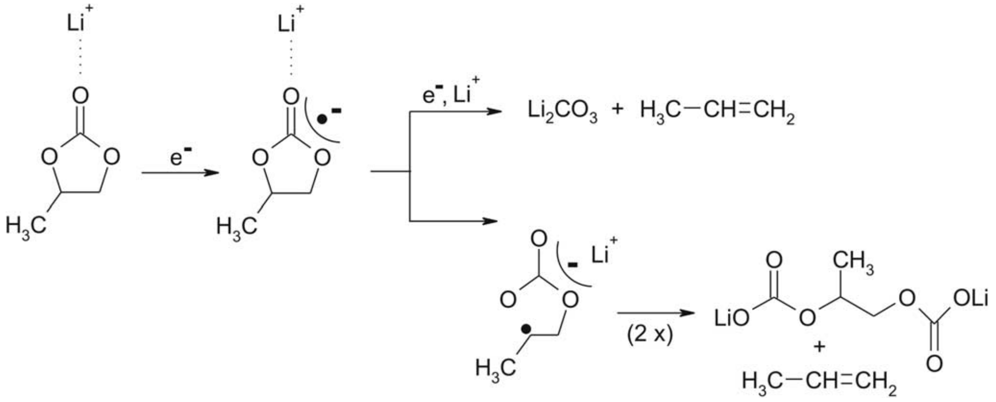
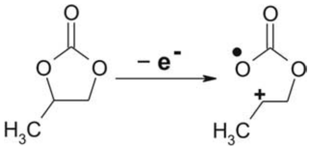


Scheme 1. Mechanism proposed for the reduction of PC on lithium and graphite surfaces (adopted from Table 6 in [3]).

On graphite, the reduction of PC commences at around 1.5 V vs. Li/Li$^+$. However, a stable SEI is only formed on relatively disordered carbons, while more graphitic carbons tend to co-intercalate solvent molecules; the subsequent decomposition of the solvent within the graphite matrix then causes its mechanical destruction (exfoliation) [5].

The onset of significant oxidation of PC/Li-salt based electrolytes on most electrode materials lies significantly above 4.0 V vs. Li/Li$^+$, with the only gaseous product being CO_2. Oxidation is proposed to proceed via the intermediate shown in Scheme 2 [3]. Subsequently, this radical species may release CO_2 and dimerise or polymerise. Accordingly, a large variety of non-volatile organic products has been proposed, for instance polycarbonates, polyethers, and alkyl carbonates (as for the reductive decomposition) [3]. The precise nature of these compounds, and the mechanisms of their formation are not yet clear. However, the existence of a passivating layer on the oxide electrode in Li batteries, resembling the SEI on the graphite electrode, is very likely [3].

Only few reports exist on the electrochemical stability of tetraalkylammonium salts in PC. Eggert and Heitbaum [6] investigated the electrolysis process on Pt in situ by means of on-line mass spectrometry. They observed the reduction of $(C_4H_{10})_4NBF_4$/PC on Pt below 1.2 V vs. Li/Li$^+$ with the major gaseous reaction product being propene. Surprisingly, CO_2 was already detected at an electrode potential as low as 2.5 V vs. Li/Li$^+$. Since the CO_2 signal was only found after previous reduction (and carbonate formation), the authors suspected that CO_2 was formed in a consecutive chemical reaction from organic carbonates [6].



Scheme 2. Possible intermediate for the oxidation of PC (adopted from Scheme 14 in [3]).

Aurbach and Gottlieb [7] analysed the reduction products formed during bulk electrolysis of $(C_4H_{10})_4NClO_4$ in PC on a gold surface by means of NMR, FT-IR, and GC–MS. Propene and the propylene dicarbonate di-anion were identified as the main decomposition products below 1.2 V vs. Li/Li$^+$, in basic agreement with Scheme 1. However, they argued that no passivating film is formed on the Au surface, as the dicarbonate species does not precipitate with R_4N^+ (unlike with Li$^+$) [7].

2. Experimental

The measurement cell (DEMS cell) used for *on-line* gas analysis is shown in Fig. 1. Two electrodes, each with an geometric electrode area of ca. 12 cm^2, were vacuum dried (24 h, 120 °C, < 0.01 mbar) and then mounted inside an argon-filled glove box on the two opposing parts of the titanium cell body with spray glue (Spray Mount, 3 M). After assembly, the cell was filled with the electrolyte, 1 M $(C_2H_5)_4NBF_4$ in PC (Honeywell, < 20 ppm water). The electrolyte gap thickness of 1 mm was defined by a polypropylene sealing placed between the two cell body parts.

All measurements were performed in sealed cells outside the glove box at room temperature. A 0.15 mm thick PTFE-bound activated carbon film supported on a 0.03 mm thick aluminum foil was used as the electrode material. The same material was characterised in previous work [2,8].

During measurement an argon stream (ca. 5 ml/min) was purged through the head space of the cell. Any evolved gases are taken up by this argon stream, of which a small part is pumped off via a capillary into a quadrupole mass spectrometer (QMS 200 Prisma, Pfeiffer Vacuum, Germany). Details of the experimental