



Short communication

# In-operando evaluation of the effect of vinylene carbonate on the insulating character of the solid electrolyte interphase

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## ABSTRACT

The solid electrolyte interphase (SEI) is an electronic insulating layer which highly affects the performance of lithium-ion batteries, especially when electrodes with low (de-)intercalation potentials such as graphite are employed. The formation of the SEI was investigated in-operando on graphite when vinylene carbonate (VC) was present as an additive in solution using feedback-mode SECM. The potential at which the surface started to become insulating was at 0.8 V vs. Li/Li<sup>+</sup> in VC-free electrolytes, while it was at 1.3 V in VC-containing electrolytes. Nevertheless, potentials more cathodic than 0.8 V have to be reached to form a homogeneous SEI. No influence in the electronic properties of the formed SEI with different concentrations of VC was observed.

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## 1. Introduction

The formation and the stability of the solid electrolyte interphase (SEI) have a fundamental role on cycle life, irreversible charge losses, and final performances of lithium-ion batteries. The SEI is an electronic insulator and ionic conductor for Li<sup>+</sup>. This allows the (de-)intercalation of Li<sup>+</sup> in the host structure while blocking further decomposition of the electrolyte components [1–4].

The nature of the SEI highly depends on the electrolyte composition as well as the presence of impurities or additives. In order to generate a stable SEI layer by consuming a low amount of irreversible specific charge, film-forming additives are often added in small amounts to the electrolyte [5,6]. Among the most common additives used in lithium-ion batteries, vinylene carbonate (VC) forms an insoluble layer containing poly-alkyl-lithium-carbonates when the electrode is polarized at potential of around 1 V vs. Li/Li<sup>+</sup> [7,8]. This insoluble layer helps suppressing the reduction of solvent molecules and by this reduces the irreversible specific charge losses in the first cycle [7,9,10]. Nevertheless no in-depth insight into the insulating nature of the SEI formed under these conditions is available.

Scanning electrochemical microscopy (SECM) in its feedback mode of operation was already established by our group as an in-operando technique to determine the potential of the SEI formation and to evaluate the electronic insulating properties of this layer [11]. Here, we

investigate the effect of VC on the SEI formation on graphite paste electrodes in comparison to VC-free electrolyte. In particular, it was investigated at which potential the formation of an insulating protective layer occurred and, even more importantly the effect of the amount of VC on the SEI electronic character.

## 2. Experimental

In order to exclude any traces of oxygen and water, the SECM setup was integrated inside a glove box (Jacomex) filled with argon (content of O<sub>2</sub> and H<sub>2</sub>O below 1 ppm). All technical details of the employed system are given in ref [12]. For SECM measurements a platinum micro-electrode with a diameter of 25 μm was employed as SECM tip. Ferrocene (Fc) (98% Sigma Aldrich) with a concentration of 20 mM was chosen as free-diffusing redox couple in solution. The electrolyte was based on 1 M lithium perchlorate (battery grade, dry, 99.99% Sigma Aldrich) in ethylene carbonate (EC) (anhydrous 99%, Sigma Aldrich) and diethyl carbonate (DEC) (anhydrous 99.7%, Sigma Aldrich), 1:1 weight ratio. Vinylene Carbonate (VC) (99%, Sigma Aldrich) was used as additive and dissolved in the electrolyte.

All potential values are referred to a reference electrode composed of metallic lithium immersed in 1 M LiClO<sub>4</sub> EC:PC (propylene carbonate, PC, anhydrous 99%, Sigma Aldrich) solution, separated from the main body of the cell by a ceramic frit. As counter electrode a cylindrical titanium mesh (Alfa Aesar) covered with TiS<sub>2</sub> particles (99.9%, Sigma Aldrich) was used.

All measurements were carried out in a specifically developed four electrode electrochemical cell, described in [12,13]. A bipotentiostat

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was used to record the current at the microelectrode (WE2) during the polarization of the graphite paste electrode (WE1). The feedback current was recorded simultaneously after positioning the microelectrode in a known close proximity to the sample surface attained during z-approach curves. Graphite paste electrodes were prepared from SFG44 particles (TIMREX SFG44, Timcal; 85% wt.) and polyvinylene difluoride binder (15% wt.) in N-methylpyrrolidone.

The current reported for the microelectrode is the normalized feedback current, defined by the ratio of the current detected at the microelectrode,  $I_T$ , and the mass-transport limiting current,  $I_{bulk}$ , recorded with the microelectrode positioned far away from the sample surface.

### 3. Results and discussion

In order to evaluate the electronic character of the SEI in-operando, feedback mode SECM was employed as proposed previously [11–13]. The microelectrode was approached to the paste electrode surface and kept at a constant z-distance and at a constant potential equal to 20  $\mu\text{m}$  and 3.6 V, respectively. The graphite paste electrodes were potentiodynamically cycled at slow scan rates while following the evolution of the normalized feedback current at the microelectrode. All graphite electrodes were polarized from OCP to 1 V at a scan rate of 0.1  $\text{mV s}^{-1}$  and subsequently cycled twice between 1 V and 0.005 V at a scan rate of 0.02  $\text{mV s}^{-1}$ . During all the measurements, ferrocene showed an excellent stability.

#### 3.1. VC-free electrolyte

The normalized feedback current detected at the microelectrode increased upon cathodic polarization of the graphite paste electrode due to the increase in the driving force for the back reduction of the ferrocenium ion ( $\text{Fc}^+$ ) at the sample surface (Fig. 1a). Once a potential of 0.8 V was reached, the normalized feedback current started decreasing. This phenomenon is attributed to the formation of an insulating

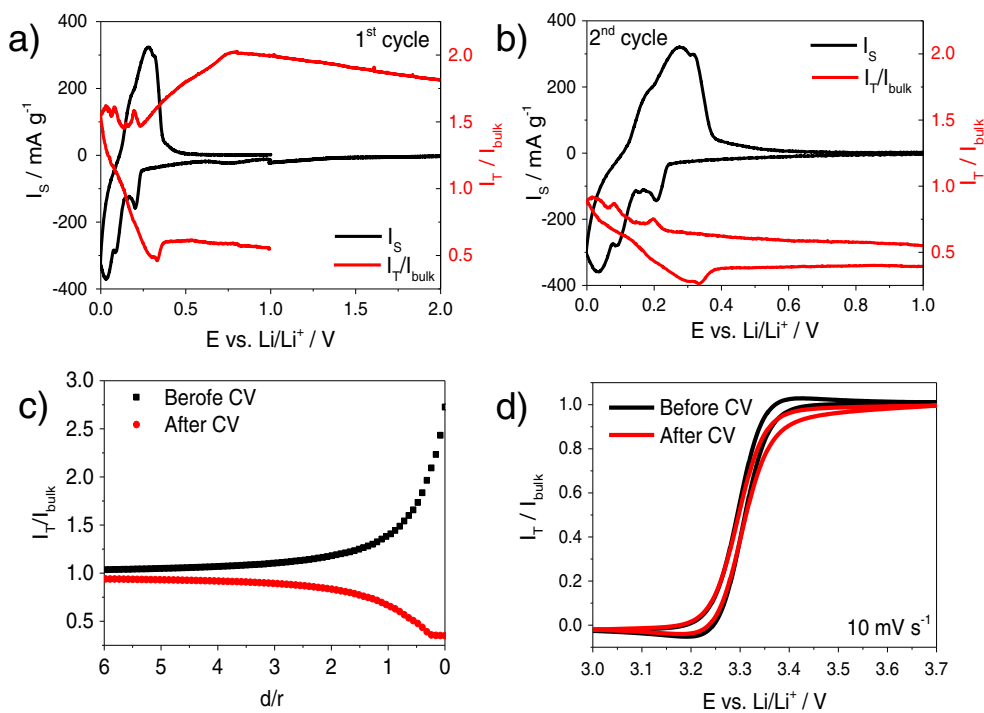
layer on the graphite surface in accordance to what was found previously for glassy carbon electrodes [13]. The normalized feedback current was affected not only by the presence of the formed SEI, but also by the (de-)intercalation of lithium ions from/in the graphite electrode. The intercalation process led to a local depletion of  $\text{Li}^+$  in front of the paste electrode due to the too slow diffusional mass transport under these conditions. As a consequence, the transference number of the  $\text{Fc}/\text{Fc}^+$  increased leading to a more predominant effect of the electric field on the normalized feedback current [12]. When  $\text{Li}^+$  were deintercalated from the graphite, the solution in front of the paste electrode was refilled with supporting electrolyte, i.e.  $\text{Li}^+$ . Thus the transference number of the redox couple as well as the normalized feedback current decreased again.

Upon cycling, the SEI became more insulating, as shown in the second cycle (Fig. 1b), where the normalized feedback current remained below unity, in accordance to what previously observed on glassy carbon [13]. Fig. 1c shows the z-approach curves before and after the polarization of graphite, confirming the presence of an insulating layer. No fouling of the microelectrode occurred during the experiment (Fig. 1d).

#### 3.2. VC-containing electrolyte

A fresh graphite paste electrode was cycled in a solution containing 2% vol. of VC. As shown in Fig. 2a, the normalized feedback current started to decrease at a potential around 1.3 V instead of 0.8 V. This further supports the fact that the decomposition of VC occurs at an earlier stage as compared with other carbonates, like EC or DEC, as previously observed by Aurbach et al. [7]. A gradual decomposition of the salt and the solvents in a potential range from 1.6 V to 0.5 V was observed in a VC-containing electrolyte by means of microgravimetry using an electrochemical quartz crystal microbalance.

We could demonstrate for the first time that the decomposition of VC also leads to the formation of an electronically insulating layer. The resulting SEI is stable as confirmed by the normalized feedback current



**Fig. 1.** VC-free electrolyte: 20 mM Fc 1 M  $\text{LiClO}_4$  in EC:DEC (1:1 %wt.). a), b) Cyclic voltammogram of the SFG44 graphite paste electrode, two cycles, and the normalized feedback current at the microelectrode held at 3.6 V; c) z-approach curves ( $r$ : radius of the microelectrode, 12.5  $\mu\text{m}$ ;  $d$ : tip-to-sample distance) to the graphite paste electrode surface before and after the experiment. d) Cyclic voltammograms at the microelectrode, scan rate: 10  $\text{mV s}^{-1}$ , in the bulk of the solution, before and after the experiment.

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