



# Investigations on the electrochemical decomposition of the electrolyte additive vinylene carbonate in Li metal half cells and lithium ion full cells



Yunxian Qian<sup>a,1</sup>, Carola Schultz<sup>a,1</sup>, Philip Niehoff<sup>a</sup>, Timo Schwieters<sup>a</sup>, Sascha Nowak<sup>a</sup>, Falko M. Schappacher<sup>a,\*</sup>, Martin Winter<sup>a,b,\*\*</sup>

<sup>a</sup> Westfälische Wilhelms-Universität Muenster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstr. 46, 48149, Muenster, Germany

<sup>b</sup> Helmholtz Institute Muenster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstr. 46, 48149, Muenster, Germany

## HIGHLIGHTS

- Different mechanisms for VC as electrolyte additive in Li metal half and Li ion full cells.
- Consumption of VC and electrolyte in half cells at the Li metal leads to rapid electrolyte aging.
- High stability of the formed SEI at the anode in full cells inhibits the further electrolyte aging.
- Correlation of CEI and SEI growth with VC consumption by XPS and HPLC.

## ARTICLE INFO

### Article history:

Received 7 July 2016

Received in revised form

14 September 2016

Accepted 18 September 2016

### Keywords:

Vinylene carbonate (VC)

Electrolyte additives

X-ray photoelectron spectroscopy (XPS)

High performance liquid chromatography (HPLC)

Cathode electrolyte interphase (CEI)

## ABSTRACT

In this study, the decomposition of vinylene carbonate (VC) additive and its effect on the aging behavior is investigated in Li metal half cells and lithium ion full cells. Four electrolyte systems, the reference electrolyte with three VC additive amounts, i.e., 1, 5 and 10 vol% are examined with commercial  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC 111) cathode material and mesophase carbon microbeads (MCMB) anode material. The thickness changes of the cathode electrolyte interphase (CEI) and of the solid electrolyte interphase (SEI) after 5 constant current cycles at 0.1C and 200 constant current/constant voltage (potential) cycles at 1C are investigated for cells containing different amounts of VC. With the help of X-ray photoelectron spectroscopy (XPS) and high-performance liquid chromatography (HPLC), a correlation between CEI thickness change and electrolyte decomposition is figured out. The addition of VC leads to a thin CEI layer and a high capacity retention in a lithium metal half cell. A strong dependence of the performance on the VC concentration is found for half cells that results from the continuous consumption of electrolyte and the electrolyte additive at the Li metal counter electrode. In contrast, for full cells, even 1 vol% of VC helps to form both a stable CEI and SEI, while a larger amount of VC increases the CEI thickness, electric contact loss and the internal resistance.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Lithium ion batteries (LIBs) are the commercial power system of choice for portable consumer electronics. They offer a high specific

energy (Wh/kg) and a high energy density (Wh/l) together with adequate power, life and safety [1,2]. The high energy contents result from the large cell voltage, i.e., a large potential difference between the cathode and the anode, which is enabled by the use of aprotic non-aqueous electrolytes [3–5]. To improve the lifetime and safety of lithium ion batteries, it is important to gain more knowledge about the reactions between electrolytes and electrode materials [6]. In general, the most commonly used components in a lithium ion battery are a lithium metal oxide cathode, a graphitic carbon based anode and a polyolefin-based separator that is placed in between and soaked with electrolyte [4]. The organic electrolyte

\* Corresponding author.

\*\* Corresponding author. Helmholtz Institute Muenster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstr. 46, 48149, Muenster, Germany.

E-mail addresses: [falko.schappacher@uni-muenster.de](mailto:falko.schappacher@uni-muenster.de) (F.M. Schappacher), [martin.winter@uni-muenster.de](mailto:martin.winter@uni-muenster.de) (M. Winter).

<sup>1</sup> Those authors contribute equally to this paper.

is a mixture of cyclic alkyl carbonates like ethylene carbonate (EC) and linear dialkyl carbonates such as ethyl methyl carbonate (EMC) or dimethyl carbonate (DMC) that lower the electrolyte viscosity [7]. As the conducting salt, lithium hexafluorophosphate ( $\text{LiPF}_6$ ) is the most used commercial salt in LIB electrolytes [8,9]. However, during cell aging,  $\text{LiPF}_6$ , which is in equilibrium with  $\text{PF}_5$  and  $\text{LiF}$ , induces the decomposition and the conversion of the organic carbonates by reacting with  $\text{PF}_5$  [10–12]. Via transesterification, for example, EMC reacts to DMC and DEC (diethyl carbonate) [13]. Hence, in an EC/EMC based electrolyte, the formation amount of DMC and DEC is one indicator of the degree of aging of lithium ion batteries [14].

In a typical lithium metal or lithium ion battery system, the electrolyte is reductively decomposed on the surface of the lithium metal or the lithiated graphite since it is not thermodynamically stable. The decomposition products are deposited on the electrode surface by forming a solid electrolyte interphase (SEI) [15]. This inhibits further electrolyte reduction while preserving  $\text{Li}^+$  conduction [16]. Vinylene carbonate (VC) [17–19], as a most prominent example from the large group of vinylene group based electrolyte additives [20,21], is a common electrolyte additive that improves SEI formation [15], especially when a graphite anode is used [22]. During cycling, the VC additive is reduced at the graphite electrode at higher potentials than the electrolyte solvents and forms insoluble products. These products contribute to a better effectiveness of the SEI [18]. Lithium carboxylate ( $\text{ROCO}_2\text{Li}$ ) species are major decomposition products of alkyl carbonates and can be found in the SEI on lithiated carbon electrodes [23]. Lithium vinylene dicarbonate ( $\text{CH}_2\text{OCO}_2\text{Li}$ )<sub>2</sub> is supposed to be the most prominent decomposition product during the reduction of VC on carbon electrodes [24,25]. Ota et al. also detected the formation of lithium divinylene dicarbonate ( $\text{CH}=\text{CHOCO}_2\text{Li}$ )<sub>2</sub> and lithium divinylene dialkoxide ( $\text{CH}=\text{CHOLi}$ )<sub>2</sub> in the corresponding SEI when adding VC to the electrolyte [22].

Aurbach et al. claimed that the presence of VC in the EC/DMC  $\text{LiPF}_6$  electrolyte reduces the irreversible capacity loss in the 1<sup>st</sup> cycle of the lithium metal based half cells and improves their stability during the prolonged cycling. This is explained by the double bond of VC whereby the molecule itself is more tensed and thus more reactive than EC. Hence, in the given electrolyte composition, VC is the most reactive species at the electrodes at low potentials and is reduced earlier than EC during the SEI formation process, protecting the electrolyte against further decomposition [22,23]. Ota et al. investigated the gas evolution during formation of the SEI layer after the first charging process. They showed that the amount of gases in EC-based electrolytes is reduced by adding VC. Further, they claimed that VC suppresses the thickness increase in the SEI layer created in the presence of EC. During reduction, VC is able to form polymeric surface species due to the further polymerization of the double bond-containing reduction products of VC. This has been considered as a promising advantage, as polymer containing surface films are expected to be more cohesive and flexible and hence provide a better surface passivation [22,23,26].

Compared to the SEI, the CEI has received far less attention by R&D concerning its presence, structure and formation mechanism [3], even though lots of CEI components are known [27–29]. The CEI formation process on the cathode surface and the SEI formation on the surface of the graphitic anode differ from each other. Due to the high oxidation ability of the cathode, the electrolyte components near the interface undergo oxidation reactions [3]. For instance, unsaturated cyclic ethers or lactones are preferentially oxidized at the cathode. They form an effective CEI that inhibits further oxidative decomposition of the electrolyte at the cathode [30]. Residual  $\text{Li}_2\text{CO}_3$ , which exists on most lithium transition metal oxide based cathodes, reacts with  $\text{LiPF}_6$ /organic carbonate

electrolytes and results in the deposition of organic electrolyte decomposition products [31–33]. An oxidation mechanism involving a single-electron transfer process that produces a cation radical from the carbonate solvent has been proposed [34]. Subsequent decomposition leads to products that form a CEI layer on the cathode. Aurbach et al. correlated the thickness with the results from the electrochemical impedance spectroscopy (EIS) [27]. They found a continued growth of the layer during prolonged cycling. It has been suggested that oxidation mechanism of vinylene compounds [21], such as VC, and of isocyanates [35,36] involves the formation of radical cations and subsequent cationic polymerization. Further, Aurbach et al. suggested that the cationic polymerization of VC at the cathode surface reduces its impedance and slightly its kinetics by a suppression of surface reactions [23]. Burns et al. varied the concentration of VC in wound Li-ion cells [37]. They observed a better lifetime for the cell adding 6 wt% VC into the electrolyte, while on the other hand, they also detected an impedance increase in the cells with more than 2 wt% of VC additive.

In this work, VC decomposition and thus consumption, and the thickness of CEI are investigated in both Li metal half cells and lithium ion full cells. 1, 5 and 10 vol% of VC are added into the electrolyte of 1.0 M  $\text{LiPF}_6$  in EC: EMC = 3:7 (quoted as LP57 in the following text). The conductivity of the different electrolytes is determined and the electrochemical performance of the corresponding cells is analyzed. The electrochemical investigation is completed with the help of self-assembled lithium ion battery T-half cells and pouchbag full cells.  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC 111) is used as the cathode material, while mesophase carbon microbeads (MCMB) is used as the anode material. Initially, the cells are cycled with the constant current (CC) of 0.1C for 5 cycles (the formation process, i.e., formation of the SEI and CEI) and then cycled under a constant current/constant voltage (CC/CV) or under a constant current/constant potential (CC/CP) regime at 1C for 200 cycles to investigate the long-term cycling performance. After cycling, the thickness of the CEI and SEI are determined by X-ray photoelectron spectroscopy (XPS), which has been proven to be a powerful method for this kind of investigation [38]. High-performance liquid chromatography (HPLC) equipped with an UV/VIS detector, which is very sensitive to double bonds like in VC, is used for the separation and quantification of the organic carbonates in the electrolyte [39]. A correlation between CEI thickness change and VC consumption in lithium ion batteries (half and full cells) that contain electrolytes with a varying VC content is figured out.

## 2. Experimental

### 2.1. Sample preparation

Commercially available NMC-111 and MCMB electrodes were used as the cathode and the anode materials. The purchased electrodes were punched into disks with a diameter of 12 mm for half cells and squares with a size of 3 cm × 3 cm for full cells. The average mass loadings were 14.6 mg/cm<sup>2</sup> for the NMC cathodes with 93% of active material and 9.0 mg/cm<sup>2</sup> for the MCMB anode with 90% of active material. For both electrodes, PVDF was used as binder and conductive carbon was added. Li metal electrodes (Rockwood Lithium, battery-grade, USA) were adopted as the counter electrode (CE) and the reference electrode (RE) for half cells. As electrolyte, 1 mol dm<sup>-3</sup>  $\text{LiPF}_6$  dissolved in 3:7 (wt%) EC: EMC mixture (BASF, Germany) was used, which is quoted as LP57. 120 μL (on the CE side), 50 μL (on the RE side) and 300 μL of the electrolyte were added into the three-electrode Swagelok T-half cells and the two-electrode pouchbag full cells, respectively. The addition of VC (Sigma Aldrich, 99.80%, Germany) varies from 1, 5, up

Download English Version:

<https://daneshyari.com/en/article/5150111>

Download Persian Version:

<https://daneshyari.com/article/5150111>

[Daneshyari.com](https://daneshyari.com)