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2-Cyanofuran—A novel vinylene electrolyte additive for PC-based electrolytes in lithium-ion batteries

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Abstract

In this contribution, we focus on propylene carbonate (PC)-based electrolytes for lithium-ion batteries. In order to avoid solvent co-intercalation into graphite the presence of a solid electrolyte interphase (SEI) is required. This film is formed due to a film-forming species, i.e. a film-forming electrolyte additive. In this contribution, we focus on a vinylene compound, 2-cyanofuran (2CF) which proves to perform well in propylene carbonate electrolytes. 2CF is investigated by in situ Fourier transform infrared (FTIR) spectroscopy in a specially developed IR cell. We conclude that the cathodic reduction of the vinylene groups (=via reduction of the double bond) in the electrolyte additive is the initiating, and thus an important step of the SEI formation process. The possibility of an electropolymerization reaction of the vinylene monomers in the used electrolytes is critically discussed on the basis of the obtained IR data.

Keywords: Lithium-ion batteries; Electrolyte additives; Solid electrolyte interphase; SEI; In situ FTIR; Electrochemical polymerization

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1. Introduction

Lithium-ion batteries operate beyond the thermodynamic stability of the used aprotic organic electrolyte, and electrolyte decomposition occurs at both electrodes. Therefore, the electrolyte has to be composed in a way that the electrolyte decomposition products form a film on the electrodes, which stops the decomposition reactions, but is still permeable to the Li^+ cations being the charge carriers.

In case of standard ethylene carbonate (EC)-based electrolytes, EC is responsible for this film formation. Propylene carbonate (PC) is another cyclic carbonate that could be suitable for application in lithium-ion batteries due to its high ion dissociation ability and good low-temperature properties, but unfortunately it is not compatible with graphite anodes. Fig. 1 shows the cyclic voltammogram of a KS 6 graphite composite electrode in 1 M $LiClO_4$ in PC. The non-desired co-intercalation of PC molecules into graphite results in subsequent reduction of PC which causes heavy gassing, and thus shedding of the graphene layers, and subsequent exfoliation of the graphite matrix [1,2]. As shown in Fig. 1, the reduction of PC starts at approximately 0.86 V versus Li/L^+, thereafter intense reduction currents occur which leads to the afore described destruction of the electrode.

The application of pure PC electrolytes requires the presence of a film-forming species, e.g. a film-forming electrolyte additive. In the presence of compounds containing vinylene groups, for example, an effective solid electrolyte interphase (SEI) is formed even when small (=additive) amounts of the "vinylene additive" are present; ~1 vol.% is still effective [3]. The principle of the cathodically (i.e. by electrochemical reduction) induced polymerization of vinylene compounds is shown in Fig. 2. Acrylonitrile was found to efficiently suppress PC-decomposition even when present at only 1 vol.% in a pure PC electrolyte [3]. During the first charge, it is reduced and contributes to the formation of a protective SEI layer. Other prominent vinylene compounds are vinylene acetate (VA) or vinylene carbonate (VC).

In this contribution, we focus on the vinylene compound 2-cyanofuran (2CF) which performs well in PC electrolytes, too.

For the future design of additives, the understanding of the electrochemical reduction and SEI formation processes is

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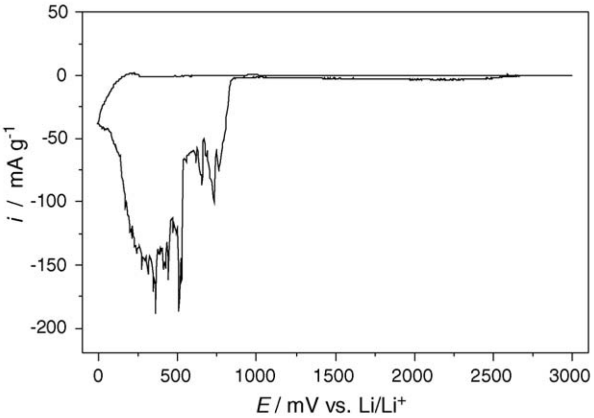

Fig. 1. Cyclic voltammogram of a KS 6 graphite composite electrode in 1 M $LiClO_4$ in PC, scan rate 50 $\mu V\ s^{-1}$.

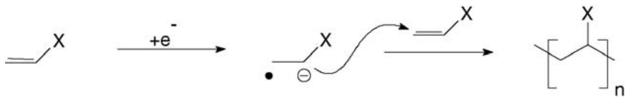

Fig. 2. Cathodic, i.e. by reduction-induced polymerization of vinylene monomers. *X* denotes an electronegative substituent (e.g. –CN).

essential. To monitor changes at the electrode/electrolyte interface during electrochemical reduction which may be correlated with the electrolyte reduction and SEI formation mechanisms, we have applied the method of in situ Fourier transform infrared spectroscopy (in situ FTIR). We particularly focus on PC- and tetrahydrofuran (THF)-based electrolytes with and without 2CF in order to elucidate both, the effect of various electrolyte additives and of various base electrolyte solvents on the obtained IR results.

2. Experimental

Propylene carbonate (Merck or Honeywell, battery grade), $LiClO_4$ (Mitsubishi Chemical Corp., battery grade) and 2-cyanofuran (Aldrich, 99%) have been used as received without further purification. THF (Aldrich) has been distilled in the presence of Na before use. Electrolyte preparation and cell assembly have been accomplished under dry argon atmosphere in a glove box. A single compartment cell with four electrodes is used for cyclic voltammetry (CV) and charge/discharge (C/D) experiments. Lithium metal is used for both counter and reference electrodes. Graphite-based anodes were made from TIMREX® SFG 44 and KS 6 synthetic graphites (Timcal AG) and used as working electrodes. In order to prepare the electrodes, a slurry of the respective graphite suspended in a solution of poly(vinylidene)fluoride (PVdF) (Aldrich) in 1-methyl-2-pyrrolidinone (Aldrich) was spread on a stainless steel current collector, dried at 120 °C overnight, then pressed at 100 kg cm^{-2}, and finally dried under vacuum at 120 °C for 6 h again. The electrodes contained 4 wt.% of PVdF binder.

$LiCoO_2$-based cathodes were made from 91 wt.% $LiCoO_2$ (Allied Signal), 6 wt.% KS 6 graphite and 3 wt.% PVdF. The preparation of the cathodes was carried out as described for the anodes, titanium mesh was used as current collector.

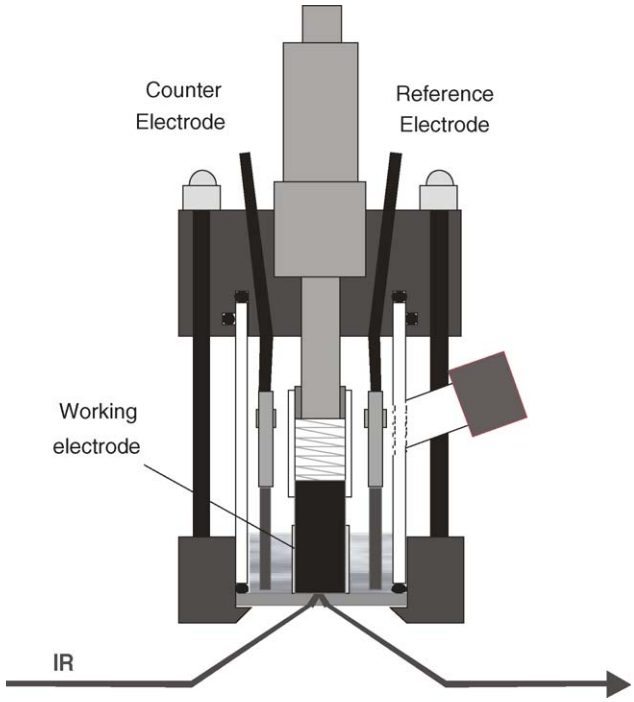

Fig. 3. Schematic view of the used FTIR cell for in situ electrochemical studies of thin-layer electrolytes. The one-compartment cell is provided with a plane optical ZnSe window. The working electrode is a 12-mm diameter cleaned and polished glassy carbon electrode which has a good capability for IR beam reflection. Metallic lithium is used as reference and counter electrode.

Cyclic voltammetry has been performed with a home-built potentiostat with a scan rate of 50 $\mu V\ s^{-1}$ in the potential range of 3000–400 mV versus Li/Li^+. For constant current cycling experiments, a potentidynamic step from 3 to 0.5 V versus Li/Li^+ (scan rate 50 $\mu V\ s^{-1}$) is followed by charge/discharge cycling at defined current of 50 mA g^{-1}.

In situ FTIR experiments have been performed in a self-developed IR-cell shown in Fig. 3. The thin-layer, one-compartment cell is provided with a plane optical ZnSe window. The working electrode is a 12-mm diameter cleaned and polished glassy carbon electrode mounted on a micrometer screw. Glassy carbon electrode surface has a good capability for IR beam reflection. The electrode is insulated with a PTFE jacket. Metallic lithium is used as reference and counter electrode. The cell is dried, assembled, filled with electrolyte and hermetically sealed in the glove box before adjusting it into the FTIR instrument. Prior to the measurements, the electrode is precisely pushed against the optical window, and the position of both the cell and the mirrors is adjusted to get a maximum reflection of the IR beam. This means that a thin-layer of electrolyte is formed between the GC electrode and the ZnSe window. A reference spectrum $R_0(\nu)$ is measured at open circuit potential (∼3 V versus Li/Li^+) before electrochemical reaction. Thereafter, the potential of the working electrode is decreased stepwise from 3 to 0.4 V versus Li/Li^+. Each spectrum is measured after a rest period of 5 min at the given potential.