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.
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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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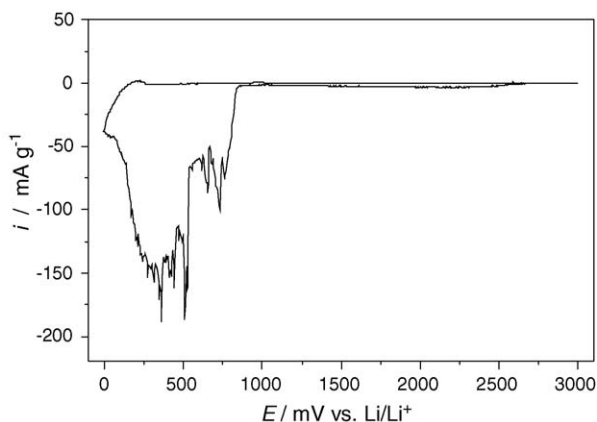
Fig. 1. Cyclic voltammogram of a KS 6 graphite composite electrode in 1 M LiClO$_4$ in PC, scan rate 50 μV s^{-1}.
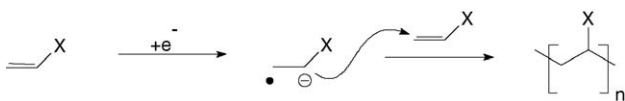

Fig. 2. Cathodic, i.e. by reduction-induced polymerization of vinylene monomers. X denotes an electronegative substituent (e.g. –CN).

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
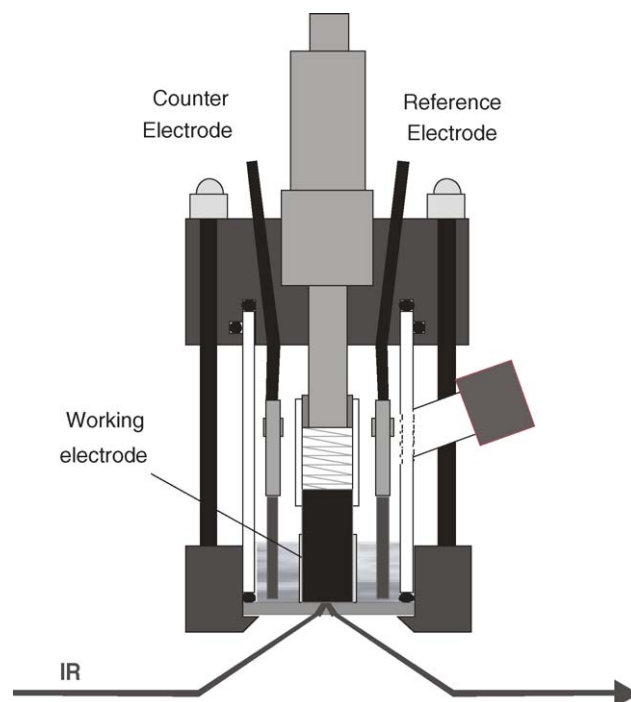

Fig. 3. Schematic view of the used FTIR cell for in situ electrochemical studies of thin-layer electrolytes. The one-compartment cell is provided with a plane optical ZnSe window. The working electrode is a 12-mm diameter cleaned and polished glassy carbon electrode which has a good capability for IR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

preparation of the cathodes was carried out as described for the anodes, titanium mesh was used as current collector.

Cyclic voltammetry has been performed with a home-built potentiostat with a scan rate of 50 μV 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 μV 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 ($\sim$3 V versus Li/Li$^+$) before electrochemical reaction. Thereafter, the potential of the working electrode is decreased stepwise from 3 to 0.4 V versus Li/Li$^+$. Each spectrum is measured after a rest period of 5 min at the given potential.
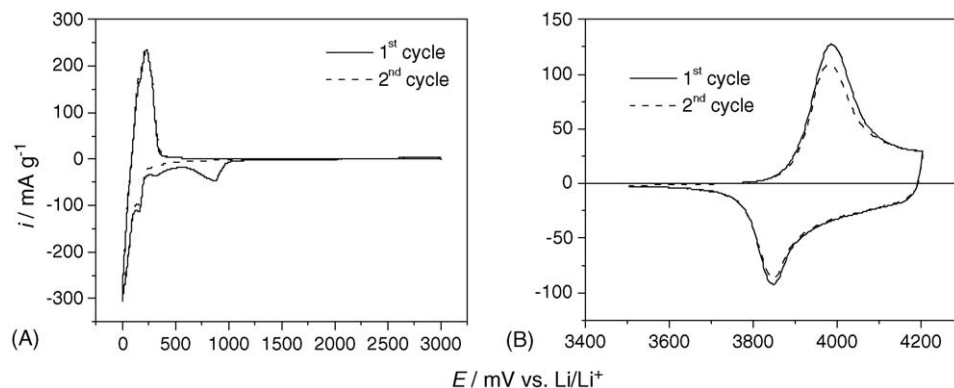
Fig. 4. Cyclic voltammogram of (A) KS 6 graphite composite electrode; (B) LiCoO₂ composite electrode in 1 M LiClO₄ in PC/2CF (99:1, v:v), scan rate 50 μV s⁻¹.

For the electrochemical experiments, an EG&G potentiostat, model 263A, is used. Spectra are measured at a resolution of 4 cm⁻¹ by accumulating six scans with a Perkin-Elmer spectrum one spectrometer equipped with a DTGS detector. The additive compound 2CF was used at a concentration of 10 vol.% added to a 0.5 M LiClO₄/THF electrolyte solution.

3. Results

3.1. Cyclic voltammetry and charge/discharge experiments

2-Cyanofuran (2CF) is an unsaturated five ring featuring the nitrile group in α-position to the double bond. The cyclic voltammogram of 2CF (1 vol.% in 1 M LiClO₄/PC) illustrates that its film formation begins at 1 V versus Li/Li⁺, the SEI formation is efficient, enabling reversible lithium intercalation/deintercalation. The filming reaction seems to be completed after the first cycle (Fig. 4A). In addition to its beneficial film-forming behavior on graphite, the 1 M LiClO₄/PC:2CF (99:1, v:v) allows the use of "4 V" cathodes due to its oxidation stability and/or the formation of a protective film at the cathode/electrolyte interface. Voltammetric measurements at a LiCoO₂ electrode verify an electrochemical window sufficient for operation in lithium-ion batteries (Fig. 4B).

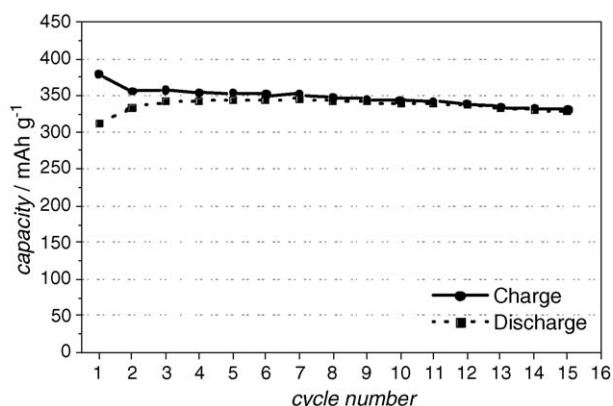Constant current C/D data confirm this beneficial behavior of 2CF (Fig. 5).

3.2. In situ FTIR studies

In order to get a deeper understanding of the way how 2CF is reduced during the first charge, in situ FTIR experiments were performed. In order to use a carbon electrode with an IR reflecting surface for the commonly in lithium-ion cells used graphite, a glassy carbon electrode (GC) was used as a model electrode. Due to the fact, that the band resolution in the fingerprint area seems to be higher in the THF-than in the PC-based electrolyte, the measurement was carried out with 1 M LiClO₄/THF as base solvent [4].

The change of the IR bands characteristic for 2CF has been monitored in parallel (in situ) to the electrochemical reduction process of the GC electrode. Fig. 6 shows the IR spectra of (i) 0.5 M LiClO₄/THF and (ii) of 2CF in 0.5 M LiClO₄/THF at a potential of 3 V versus Li/Li⁺. IR bands which are characteristic of the respective additive are indicated by (*).

To emphasize the changes of the characteristic IR bands during the reduction in a more visible way, we took advantage of the subtractively normalized intercacial FTIR spectroscopy (SNIFTIRS) method [5]. Basically, the SNIFTIRS method relates the spectrum measured at the applied potential

Fig. 5. Charge and discharge capacities of graphite (SFG 44) in 1 M LiClO₄ in PC/2CF (99:1, v:v), potentiodynamic/constant current cycling at ±50 mA g⁻¹.
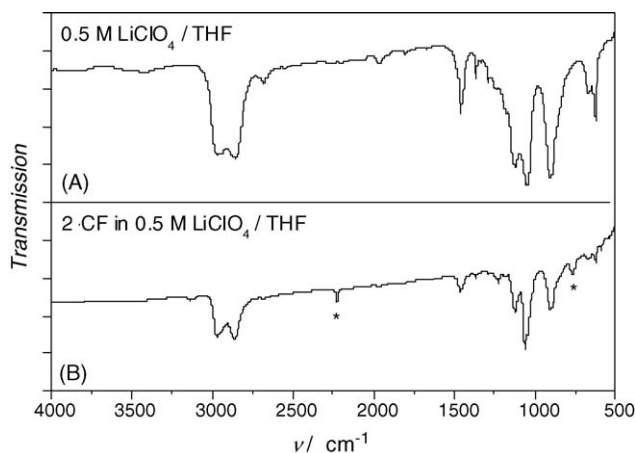

Fig. 6. In situ FTIR spectra of 2CF (10 vol.%) in 0.5 M LiClO₄/THF at the glassy carbon electrode before electrochemical reaction at open circuit potential (IR bands characteristic for the respective additive are indicated by *). (A) 0.5 M LiClO₄/THF. (B) 2CF in 0.5 M LiClO₄/THF.
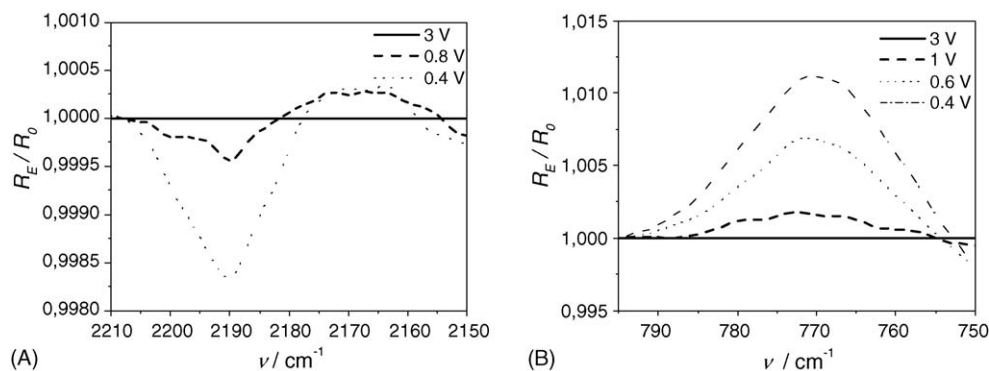
Fig. 7. Detailed SNIFTIRS spectra of 2CF (10 vol.%) in 0.5 M LiClO$_4$/THF. (A) Bands at ~2190 cm^{-1} represent an increase of concentration of saturated C≡N stretching vibration of nitriles during electrochemical reduction; bands at ~2170 cm^{-1} represent a decrease of concentration of unsaturated C≡N stretching vibration of nitriles during electrochemical reduction. (B) Bands at ~770 cm^{-1} represent a decrease of concentration of aromatic C–H out-of-plane bending.

$R_E(\nu)$ to the reference spectrum $R_0(\nu)$ recorded at open circuit potential, by using the following equation: $R(\nu) = R_E(\nu)/R_0(\nu)$, where ν denotes the wave number. Selected SNIFTIRS spectra well representative for the electrochemical processes in the IR cell are shown in Fig. 6. In the SNIFTIRS mode, positive bands indicate a decrease in concentration and negative bands indicate an increase in concentration of the chemical species represented by the band.

The filming reaction of 2CF proceeds via a reduction of the vinylene double bond. This has an impact on (i) the C≡N stretching vibration (due to reduction there is a change from an unsaturated nitrile containing the vinylene group to a saturated one) and on (ii) the C–H out-of-plane vibration of the aromatic ring. The SNIFTIR spectra shown in Fig. 7 confirm that 2CF reacts along with a reduction of the vinylene double bond. The peak of C≡N stretching vibration of the saturated nitrile (~2190 cm^{-1}) increases and the peak of the unsaturated nitrile (~2170 cm^{-1}) decreases.

Fig. 7 shows a decrease of the CH out-of-plane bending vibration peak (770 cm^{-1}) at lower potentials. This peak reduction also indicates a chemical reaction of the additive by reduction of the double bond.

4. Discussion

In summary, IR results indicate that in the investigated PC electrolyte, electrolyte reduction is initiated by reduction of the vinylene additive and that conversion of the unsaturated double bond into a saturated compound takes place during the reduction reaction. In literature, it is generally reported that the SEI is a heterogeneous mixture of electrolyte decomposition products of electrolyte components electrolyte solute, electrolyte additive or impurities. A detailed summary can be found in literature [6]. The reduction of other electrolyte species, namely LiClO$_4$, THF, or PC, could not be observed by IR spectroscopy, which shows a limitation of this method.

The view of a heterogeneous SEI is confirmed by studies investigated with the electrolyte additive acrylonitrile (AN) [3]. Its chemical structure and electrochemical behavior is related to 2CF. From X-ray photoelectron spectroscopy (XPS) analysis of the SEI formed in a PC-based electrolyte with AN [3], we know
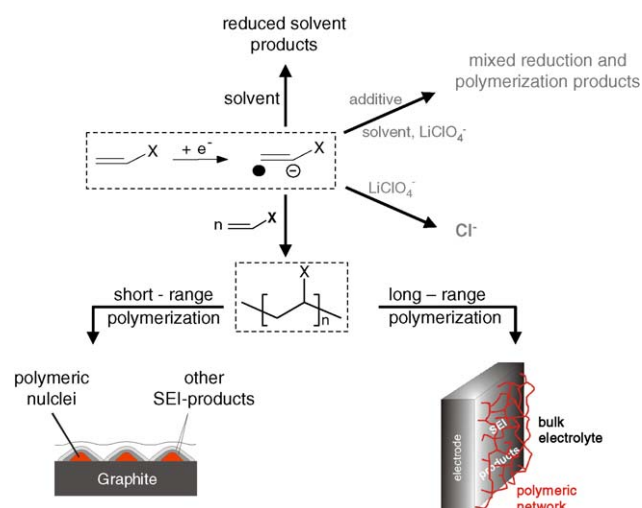

Fig. 8. Reaction scheme regarding the possible reactions of the formed radical anion with all regular electrolyte components.

that reduction products of LiClO$_4$ and PC are also incorporated in the SEI film.

A reaction scheme regarding the possible reactions of all regular electrolyte components with vinylene electrolyte additives is shown in Fig. 8. The reduction of the electrolytes is initiated by reduction of the vinylene additive, most probably forming a radical anion. Further consecutive reactions of the radical anion (i) with the base solvent, (ii) with the electrolyte solute (LiClO$_4$), (iii) with other vinylene compounds, or (iv) even with all compounds yielding mixed reduction and polymerization products are possible (Fig. 8). For example, considering statistical reasoning, a consecutive reaction of the radical anion with the solvent should be favored: as in a 1 M LiClO$_4$/PC electrolyte with 10 vol.% additive the solvent makes up more than 90 mol.% of the electrolyte in case of PC (compared to ~7 mol.% additive and 3 mol.% LiClO$_4$).[1]

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[1] The local availability to the formed radical anion depends on the local concentration of the respective electrolyte components, which may be different to the bulk ratio. For example, certain electrolyte components may be preferably located closer to the electrodes surface than others.

Depending on whether the resulting polymers have short or long polymer chain one might propose two different scenarios for participation of the polymer in the SEI. In case of short-range polymerization, it can be assumed that the polymerization products of the vinylene additive reduction form polymeric nuclei, on which SEI products from other electrolyte components grow. If long-range polymerization occurs, a polymeric network reinforces the adherence and retention of the SEI (including SEI products of other electrolyte components) at the electrode surface.

This and other possible reactions can only proceed, when the formed radical anion has the ability (reducing power) to transfer its electron to the respective electrolyte component. In addition, the possibility of other electrolyte components to react with the radical anion depends on their reduction potentials. Generally, the reaction paths illustrated in Fig. 8 again emphasize the fact that SEI products formed on graphite electrodes can be mixed products, and therefore are heterogeneous.

5. Conclusions

2-Cyanofuran (2CF) is a new vinylene group containing additive for propylene carbonate-based electrolytes investigated with graphitic anodes. The compound shows good SEI-forming behavior on graphite and suppresses solvent co-intercalation. Furthermore, the required amount of electrolyte additive to form a stable film on the electrode is very low (∼1 vol.%). Therefore, lithium-ion batteries with graphitic anodes may no longer depend on the currently used electrolyte component ethylene carbonate (EC), which suffers from a too high melting point.

Due to the results gained from in situ FTIR investigations, we propose that in the presence of 2CF, reduction of the electrolyte is initiated by reaction of the double bond of the vinylene compound. As a result, the unsaturated vinylene compound is converted into a saturated compound, which participates in the SEI. It is not clear, whether this is an electropolymerization reaction of the additive alone, i.e. without the participation of other electrolyte components. The consequence of the latter is that "mixed" reduction and polymerization products may be formed. This explanation is also in agreement with the numerous reports that claim a very heterogeneous composition of the SEI.

Acknowledgements

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