

Short communication

Ethyl isocyanate—An electrolyte additive from the large family of isocyanates for PC-based electrolytes in lithium-ion batteries

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Abstract

To avoid solvent co-intercalation into graphite, the presence of a solid electrolyte interphase (SEI) is required. This film is formed via the reductive decomposition of electrolyte species, i.e. a film forming electrolyte additives. In this contribution we focus on an isocyanate compound, ethyl isocyanate (EtNCO) which performs well in a propylene carbonate electrolyte at both graphite anode and LiCoO₂ cathode. EtNCO is investigated by in situ Fourier transform infrared (FTIR) spectroscopy. We conclude that the formation of a radical anion via electrochemical reduction of the electrolyte additive is the initiating step of the SEI formation process. The electro-polymerization of isocyanate monomers in small additive amounts in the PC electrolyte is critically discussed.

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1. Introduction

The performance of graphitic carbons as anodes in lithium-ion batteries depends on the presence of electrolyte species, which are able to establish an as far as possible electronically insulating and at the same time lithium-ion conducting solid electrolyte interphase (SEI) film. In the case of “standard” ethylene carbonate-based electrolytes, the solvent EC is responsible for SEI formation. Propylene carbonate (PC) is another cyclic carbonate that would 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 due to co-intercalation, PC-decomposition and heavy propylene gas evolution [1–6]. Combination of PC with graphite requires the presence of film forming electrolyte additives.

Electrolyte additive decomposition and SEI formation can take place via different mechanisms. One mechanism is electrochemical polymerization via reduction of vinylene

monomers. Previously, we suggested that the first step of the electrochemically induced reduction (cathodically induced electro-polymerization) of vinylene compounds is the electron transfer from the electrode to the double bond, which starts a chain reaction via addition of the formed reactive species to the double bonds of other monomers or other solvent components present in the electrolyte. Only the first electron transfer step is an electrochemical one, thus a charge consuming step. The subsequent reactions are apparently only of chemical nature [4,5].

Acrylic acid nitrile (AAN) has been presented [7,8] as a novel example from the large class of vinylene group containing film forming additives for anodes in lithium-ion batteries. The outstanding filming properties of vinylene compounds such as AAN allow using graphitic carbon anodes in PC-based electrolytes even with only 1 vol.% of the additive. 2-Cyanofurane [9] and vinylene carbonate [10], and vinylene acetate [11] are further vinylene additives.

An electro-polymerization mechanism can be also expected by using isocyanates as electrolyte additives. From early investigations in the field of preparative organic electrochemistry, the reductive polymerization of isocyanates is well known [12,13]. In this contribution, we want to focus on ethyl isocyanate (EtNCO) as electrolyte additive in a PC-based electrolyte. To

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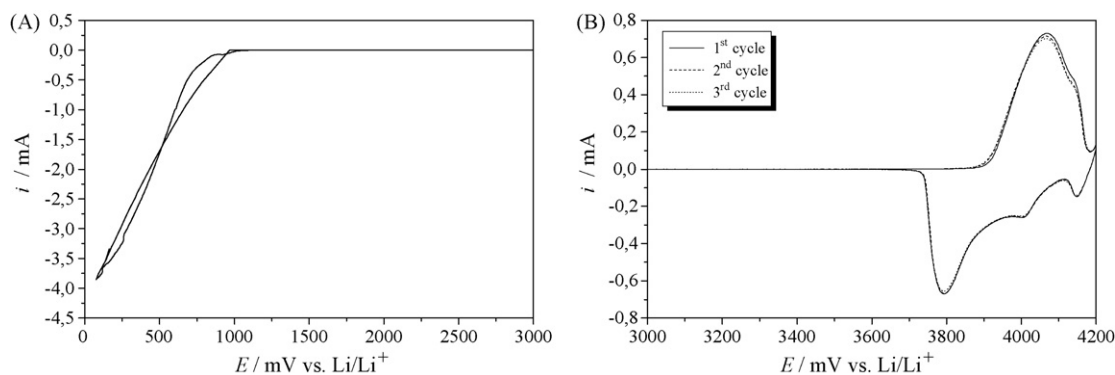


Fig. 1. Cyclic voltammograms of a MCMB electrode (A) and a LiCoO_2 electrode (B) in 1 M LiClO_4/PC , scan rate: $50 \mu\text{V s}^{-1}$.

monitor changes at the electrode/electrolyte interface which may be correlated with the electrolyte reduction and SEI formation mechanisms, we have applied in situ Fourier transform infrared (FTIR) spectroscopy.

2. Experimental

Propylene carbonate (Honeywell, battery grade), LiClO_4 (Mitsubishi Chemical Corp., battery grade) and ethyl isocyanate (ALDRICH, 99%) have been used as received. The used electrode materials were mesocarbon microbeads (MCMB 1028, Osaka Gas), LiCoO_2 (Nippon, Japan), polyvinylidene fluoride/hexafluoropropylene (PVDF/HFP) binder (Kureha Chemicals, Japan). Electrodes about $60 \mu\text{m}$ in thickness (graphite on Cu and LiCoO_2 on Al as current collectors) were prepared. The graphite electrodes contained 90 wt.% MCMB and 10 wt.% PVDF/HFP binder. The LiCoO_2 electrodes contained 90 wt.% LiCoO_2 , 5 wt.% carbon black (Super P, TIMCAL) and 5 wt.% PVDF/HFP. Electrolyte preparation and cell assembly have been accomplished under dry Ar in a glove box. A three-electrode single compartment cell has been used for cyclic voltammetric experiments. Lithium metal was used for both counter and reference electrode. Cyclic voltammetry has been performed with a scan rate of $50 \mu\text{V s}^{-1}$ in the potential range of 3000–10 mV versus Li/Li^+ .

In situ FTIR experiments have been performed in a self-developed IR-cell, described elsewhere [14]. The thin-layer, one-compartment cell is provided with a plane optical ZnSe window. The working electrode is a 12 mm diameter glassy carbon (GC) electrode. The GC surface has a good capability for IR beam reflection and therefore is used as model electrode. Metallic Li is used as reference/counter electrodes. A reference spectrum R_0 is measured at open circuit potential ($\sim 3 \text{ V}$ 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 an equilibration time of 5 min at the given potential. 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 EtNCO was used at a concentration of 10 vol.% added to 0.5 M LiClO_4/PC electrolyte solution.

3. Results

3.1. Cyclic voltammetry

If effective solid electrolyte interphase (SEI) film formation does not take place, co-intercalation and subsequent reduction of PC results in heavy gassing and finally exfoliation of graphite. The reduction of PC starts at approx. 0.9 V versus Li/Li^+ continuing with intense reduction currents (Fig. 1A). The cyclic voltammogram of a LiCoO_2 composite electrode in 1 M LiClO_4/PC in the potential range of 3.0–4.2 V versus Li/Li^+ is illustrated by Fig. 1B.

EtNCO is a saturated linear isocyanate. The cyclic voltammogram of graphite in a 1 M LiClO_4/PC electrolyte containing 2 wt.% EtNCO illustrates that SEI formation starts at 1 V versus Li/Li^+ , the SEI formation being effective and thus enabling reversible lithium intercalation/de-intercalation. The filming reaction seems to be completed after the first cycle (Fig. 2). The 1 M $\text{LiClO}_4/\text{PC}/\text{EtNCO}$ electrolyte allows also the use of the “4 V” LiCoO_2 cathode (Fig. 3).

3.2. In situ FTIR studies

The changes of the IR bands characteristic for EtNCO have been monitored in situ to the electrochemical reduction pro-

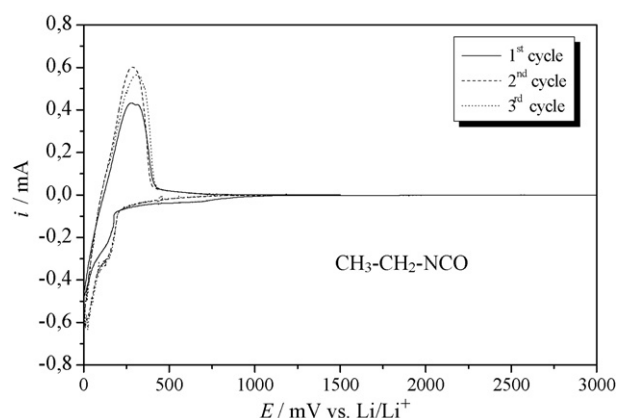


Fig. 2. Cyclic voltammograms of a MCMB graphite electrode in 2 wt.% EtNCO in 1 M LiClO_4/PC , scan rate: $50 \mu\text{V s}^{-1}$.

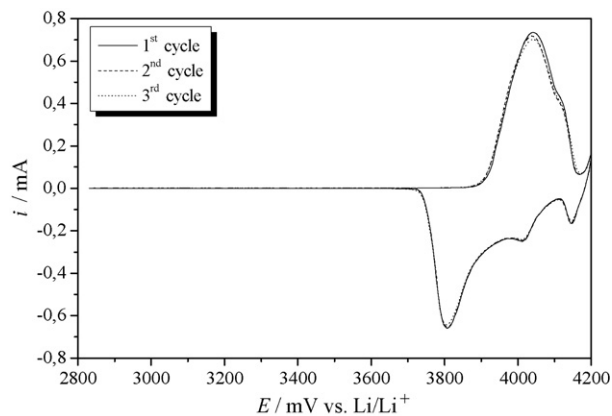


Fig. 3. Cyclic voltammograms of a LiCoO₂ electrode in 2 wt.% EtNCO in 1 M LiClO₄/PC, scan rate: 50 $\mu\text{V s}^{-1}$.

cess of the glassy carbon electrode. Fig. 4 shows the IR spectra of: (i) 1 M LiClO₄/PC and (ii) of EtNCO in 1 M LiClO₄/PC at the open circuit potential potentials, close to 3.0 V versus Li/Li⁺. The IR band at $\sim 2250\text{ cm}^{-1}$ which is characteristic of the EtNCO additive is indicated by an asterisk (*). The band represents the asymmetric –NCO stretching vibration of isocyanate compounds.

To emphasize the changes of this characteristic band during reduction in a more visible way, we took advantage of the SNIFTIRS method (subtractively normalized interfacial FTIR spectroscopy) [7]. Basically, the SNIFTIRS method relates the spectrum measured at the applied potential $R_E(\nu)$ to the reference spectrum $R_0(\nu)$ recorded at open circuit potential, by using the equation: $R(\nu) = R_E(\nu)/R_0(\nu)$, in which ν denotes the wave number. Selected SNIFTIRS spectra representative for the electrochemical processes in the IR cell are shown in Fig. 5. 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. During electrochemical reduction of the electrolyte (beginning at $\sim 1.1\text{ V}$ versus Li/Li⁺) at a glassy-carbon electrode one can observe a

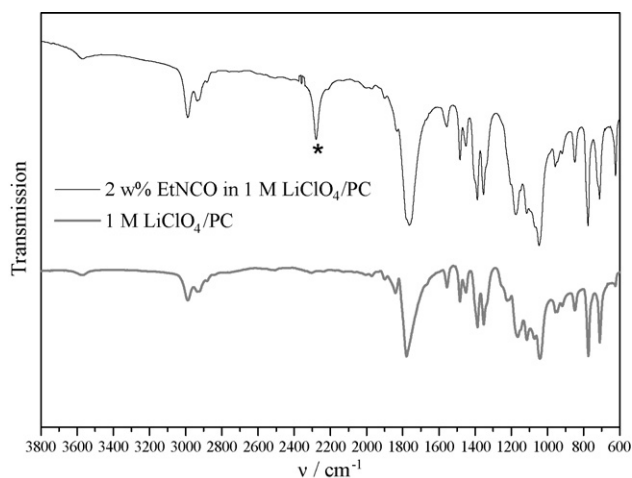


Fig. 4. Transmission FTIR spectra of EtNCO (10 wt.%) in 1 M LiClO₄/PC at a glassy carbon electrode before electrochemical reaction at open circuit potential. The band characteristic for the additive is indicated by asterisk (*).

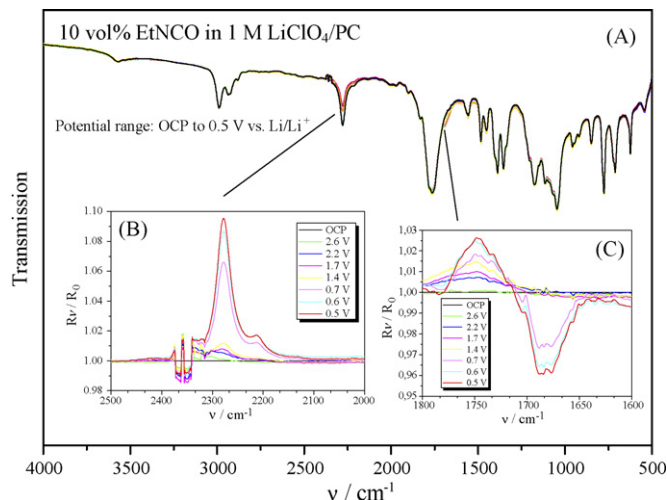


Fig. 5. (A) Transmission FTIR spectra of 10 vol.% EtNCO in 1 M LiClO₄/PC at a glassy-carbon working electrode recorded during electrochemical reduction from OCP to 0.5 V vs. Li/Li⁺. (B) Detailed SNIFTIRS spectra: band changes are indicating a decrease of asymmetric –NCO stretching vibration (2270 cm^{-1}). (C) Detailed SNIFTIRS spectra: band changes are indicating a decrease of C=O stretching vibration of esters (1750 cm^{-1}) and an increase of C=O stretching vibration of amides (1690 cm^{-1}).

decrease of the band at $\sim 2275\text{ cm}^{-1}$. This indicates that the –NCO functional group takes part in the reduction process. Furthermore, a new band appears in the FTIR spectrum in parallel. The strong band appearing at $1690\text{--}1670\text{ cm}^{-1}$ can be assigned to a C=O stretching vibration for an amide.

The band change at 1750 cm^{-1} is assigned to C=O stretching vibration of esters. Esters can result from a ring opening of PC. Obviously, the reduction of PC is not fully suppressed by the presence of the additive. On the other hand, PC co-intercalation into graphite is suppressed in presence of the additive (cf. Fig. 2). It cannot be concluded from the given data, whether this behaviour is due to the use of different electrodes: GC versus MCMB or whether this data is consistent, i.e. that some, but very much reduced PC reduction is not associated with exfoliation of graphite. The noisy signal at 2350 cm^{-1} is due to CO₂ in solution.

4. Summary and conclusion

Based on situ FTIR spectroscopy results we propose, that in the presence of EtNCO, the reduction of the electrolyte is initiated by reaction of the isocyanate group. As a result, the monomer polymerizes and the polymeric product (e.g. polyimides or cyclic isocyanurates) participates in the SEI. It is not clear, whether this is an electro-polymerization reaction of just the additive, i.e. without the participation of other electrolyte components. The consequence of the latter would be that “mixed” reduction and polymerization products may be formed. This argument is in agreement with the numerous reports that claim a heterogeneous composition of the SEI.

Learning from organic electrochemistry, the first step of the isocyanate reduction is the conversion to an intermediate radical anion (Fig. 6). This intermediate may react with: (i) another

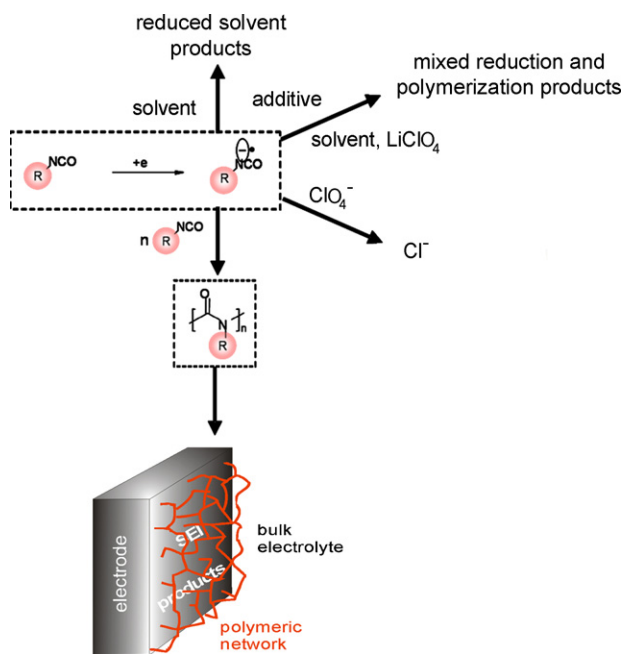


Fig. 6. Possible reaction paths of the intermediate isocyanate radical anion.

isocyanate monomer, resulting in polymerized products which participate in the SEI and (ii) with other electrolyte components (LiClO_4 , PC) which participate in the electrolyte reduction process by subsequent and/or parallel reactions and finally may also participate in the SEI.

Ethyl isocyanate is only one compound of the large family of isocyanates. From the results presented here, it can be concluded that systematic investigations will disclose further electrolyte additives of the isocyanate family. We expect that most (probably

all) of them also operate according to the electro-polymerization mechanism.

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