

Isocyanate compounds as electrolyte additives for lithium-ion batteries

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Abstract

Several isocyanate compounds have been investigated with regard to their performance as film forming electrolyte additives in propylene carbonate (PC) and EC/EMC-based electrolytes. In situ and ex situ analytical methods were applied to understand the differences in performance. Particular attention was paid to the differences of aromatic and linear isocyanate compounds.

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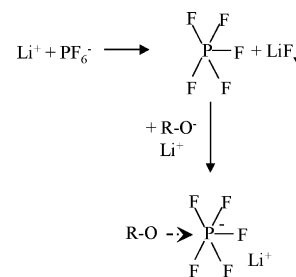
1. Introduction

For operation of graphite anodes in liquid organic and inorganic electrolytes of lithium-ion batteries, formation of a protective, but at the same time still lithium cation conductive film – the so-called solid electrolyte interphase (SEI) – is necessary. Film forming electrolyte additives are able to establish and/or enhance the SEI. Prominent additive examples include CO₂, N₂O, S_x²⁻, SO₂, chloroethylene carbonate, fluoroethylene carbonate, vinylpropylene carbonate, vinylene carbonate, catechol carbonates, 12-crown-4, ethylene sulfite [1–13], and many others. There is intense search for new electrolyte additives; often this is done by a try-and-error approach.

Here we present our recent studies on isocyanate electrolyte additives. The isocyanate functional group –NCO is known to be reactive in general. Several applications as electrolyte additive in LIBs are self-suggesting:

- (i) Monomers with –NCO functional groups can be electrochemically polymerized. The reductive polymerization to polyimides is well known from early investigations in organic electrochemistry [14,15]. Electrochemical oxidative polymerization is also possible.

- (ii) Isocyanates can act as anion receptors to improve the electrochemical and chemical stability of the electrolyte. For instance, PF₆⁻ anions are known to be thermally unstable and to decompose in the electrolyte according to:



Isocyanates acting as anion receptors form complexes with the anion and thereby can inhibit the decomposition reaction in the electrolyte. By reducing thus ion-pairing in the electrolyte, a positive side-effect is the increase of both lithium-ion diffusion and lithium transport number.

- (iii) Thermal, i.e., temperature induced, reactions also could yield polymer films. This mechanism could be used as shut-down procedure during thermal runaway, thus providing a non-reversible safety feature.
- (iv) SEI decomposition at elevated temperatures is the first reaction in a series of exothermal reactions taking place during thermal runaway. Considering that this SEI decomposition mechanism might take (partially) place via radical disintegration, the –NCO group may slow down SEI decomposition by functioning as radical trapper.

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In summary, studies on isocyanate compounds are motivated by several possible applications in LIBs. Here we report on screening studies of a number of isocyanates. Among hundreds of isocyanates we concentrated on compounds with (i) benzyl, (ii) phenyl, and (iii) linear structure with electron-donating or electron-withdrawing substituents.

2. Experimental

Propylene carbonate (Honeywell, battery grade), LiClO_4 (Mitsubishi Chemical Corp., battery grade) and isocyanate compounds (all from ALDRICH) have been used as received without further purification. The “standard electrolyte” was 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (v/v, 1:1, Merck). The electrode materials included mesocarbon microbeads (MCMB 1028, Osaka Gas), LiCoO_2 (Nippon Chemical, Japan), KS6 graphite (TIMCAL) and poly(vinylidene fluoride)/hexa-fluoropropylene (PVDF/HFP; Kureha Chemical). Carbon electrodes (on Cu current-collector) and LiCoO_2 electrodes (on Al current-collector) were prepared. The carbon electrodes contained 90 wt.% MCMB and 10 wt.% PVDF/HFP binder. The LiCoO_2 electrodes contained 90 wt.% LiCoO_2 , 5 wt.% KS6 and 5 wt.% PVDF/HFP binder. A single compartment cell with

3 electrodes was used for cyclic voltammetric experiments. Lithium metal served for both counter and reference electrodes. Cyclic voltammetry has been performed with a scan rate of $50 \mu\text{V/s}$ in the potential range of 3000–0 mV versus Li/Li^+ . For constant current cycling experiments at C/10 current, the square electrode size of the anode was $2.5 \text{ cm} \times 2.5 \text{ cm}$. The square electrode design of the cathode was $2 \text{ cm} \times 2 \text{ cm}$. The anode/cathode capacity ratio was 1.151. The theoretical capacity for this full cell design was 4.5 mAh. Celgard[®] 2400 separators were drenched with 200 μl electrolyte.

In situ FTIR experiments have been performed in a self-made IR-cell described elsewhere [16]. The cell has been provided with an optical ZnSe window. The working electrode was a 12 mm diameter glassy carbon electrode (GC) as GC has a good capability for IR beam reflection. Metallic Li was used as reference and counter electrode.

For the on-line mass spectrometry, a self-developed headspace cell was used. Graphite was used as working electrode, Li foil as counter and reference electrodes. Three Freudenberg 2226[®] separators were drenched with $\sim 150 \mu\text{l}$ of electrolyte. For the experiments presented here no carrier gas was used (the argon inlet was sealed).

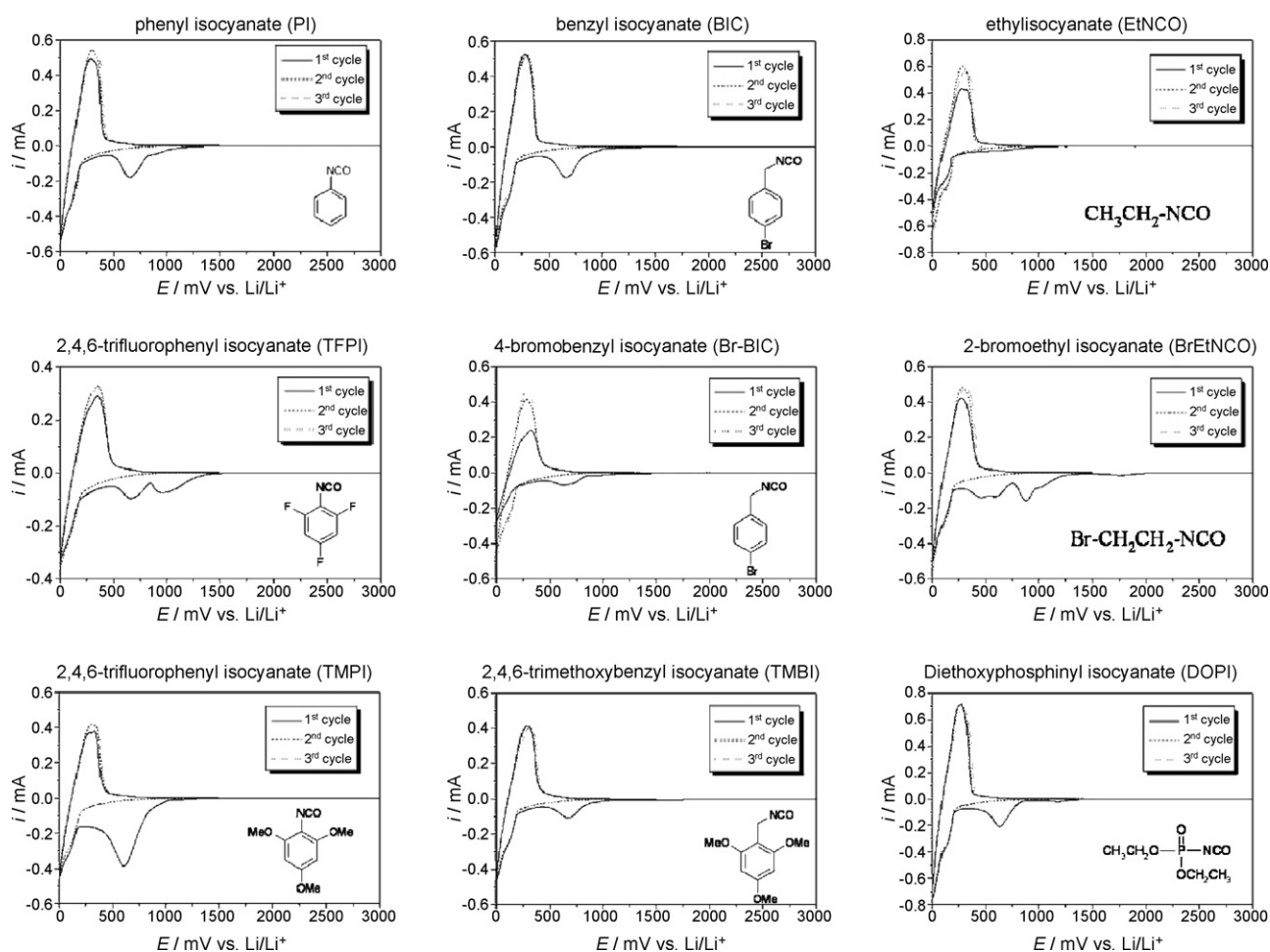


Fig. 1. Cyclic voltammograms of 2 wt.% of the respective isocyanate compound in 1 M LiClO_4/PC on a MCMB 1028 graphite anode; scan rate: $50 \mu\text{V s}^{-1}$.

3. Results and discussion

3.1. Electrochemical characterization

Isocyanate additives should be reduced at potentials well-positive to PC co-intercalation potentials. PC co-intercalation and subsequent reduction of the co-intercalated PC results in strong gassing and thus finally graphite electrodes exfoliate in PC [17,18]. Cyclic voltammograms of these compounds on MCMB graphite anodes in 1 M LiClO₄/PC are shown in Fig. 1. The onset potentials of reduction are displayed in Table 1. The cyclic voltammograms of isocyanate compounds on LiCoO₂ cathodes are shown in Fig. 3: 1 C constant current cycling; discharge capacities of pouch cells using 1 M LiPF₆/EC:DMC (v/v; 1:1) with different isocyanate compounds (2 wt.%) (Fig. 2).

The –NCO functional group obviously enhances the SEI formation on graphite. Different aromatic and linear isocyanate compounds form an SEI on graphite. The phenyl isocyanate with the functionality –OMe, abbreviated TMPI, does however not perform well. One reason might be that this functionality is electron-donating, shifting the reduction to more negative potentials, thus the additive reduction is too late to form an SEI before PC co-intercalation starts. It also appears that the additive reduction products do not form an effective SEI. This

Table 1

Reduction potentials of isocyanate compounds determined by cyclic voltammetry

	Reduction potential (V vs. Li/Li ⁺)
4-Bromobenzyl isocyanate (Br-BIC)	1.25
Benzyl isocyanate (BIC)	1.25
Phenyl isocyanate (PI)	1.62
2,4,6-Trimethoxyphenyl isocyanate (TMPI)	1.25
2,4,6-Trifluorophenyl isocyanate (TFPI)	1.45
2-Bromoethyl isocyanate (BrEtNCO)	2.00
2,4,6-Trimethyl benzyl isocyanate (TMBI)	1.25
Diethoxyphosphinyl isocyanate (DOPI)	1.47
Ethyl isocyanate (EtNCO)	1.10

is in line with the behaviour at the positive electrode. Both, aromatic isocyanates with electron-donating groups, TMPI and TMBI, suffer from strong oxidation at the LiCoO₂ cathode already at potentials below 4 V versus Li/Li⁺. We suppose that this oxidation results in formation of a resistive film on the cathode, which hinders further Li⁺ insertion/de-insertion as indicated by the “flat” and “broad” current peaks. Apparently, electrolyte additives featuring electron-donating groups within their chemical structure are not suitable for use in 4 V-lithium-

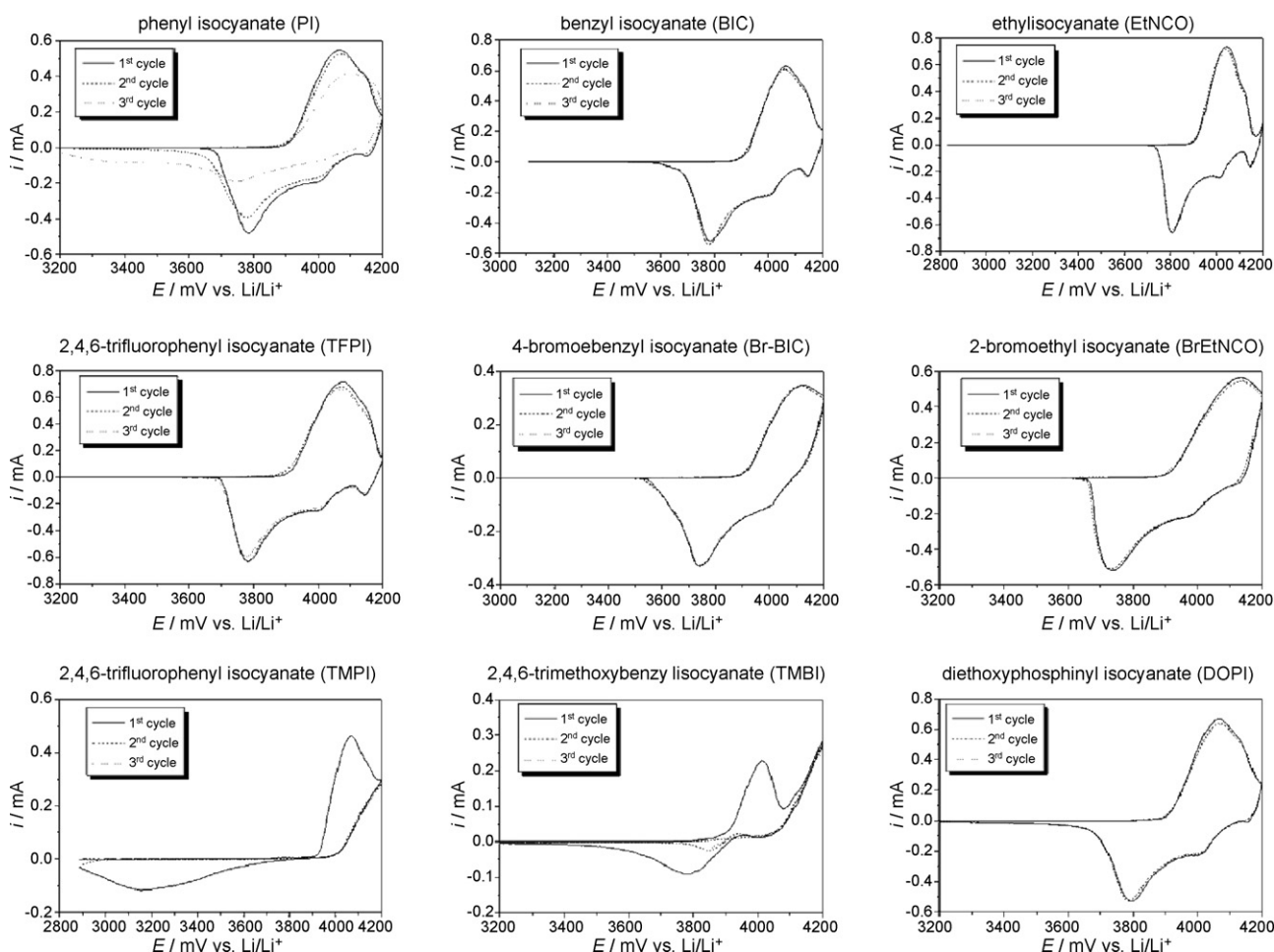


Fig. 2. Cyclic voltammograms of 2 wt.% of the respective isocyanate compound in 1 M LiClO₄/PC on a LiCoO₂ cathode; scan rate: 50 μV s⁻¹.

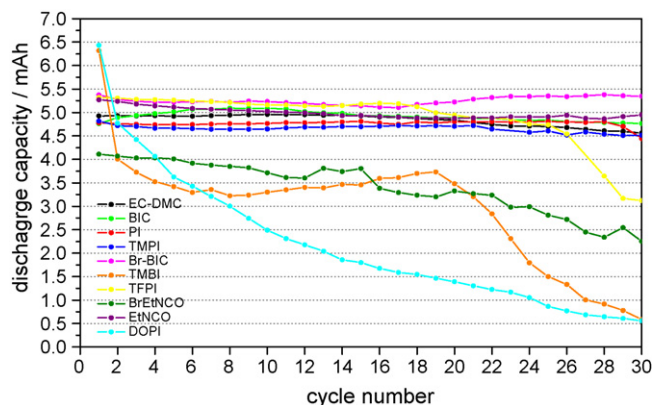


Fig. 3. 1 C constant current cycling; discharge capacities of pouch cells using 1 M LiPF₆/EC:DMC (v/v; 1:1) with different isocyanate compounds (2 wt.%).

ion batteries. On the other hand, phenyl and benzyl compounds with electron-withdrawing groups, except of Br-BIC, obviously do not have such a blocking effect (high resistance for lithium-ion transfer) at the cathode. They also effectively suppress PC co-intercalation. As a rule, the “smaller” linear isocyanates have high enough reduction potentials and the SEI is formed fast enough to suppress PC co-intercalation into graphite. The linear isocyanates also show good compatibility with the LiCoO₂ cathode.

Charge–discharge investigations were performed by adding the additives to 1 M LiPF₆/EC:DMC (v/v, 1.1) in pouch cells. Discharge capacities are shown in Fig. 3. EtNCO, BIC, and Br-BIC seem to improve the cell performance compared to the EC:DMC electrolyte.

The obvious differences of the SEI films formed in electrolytes containing linear and aromatic isocyanates have been

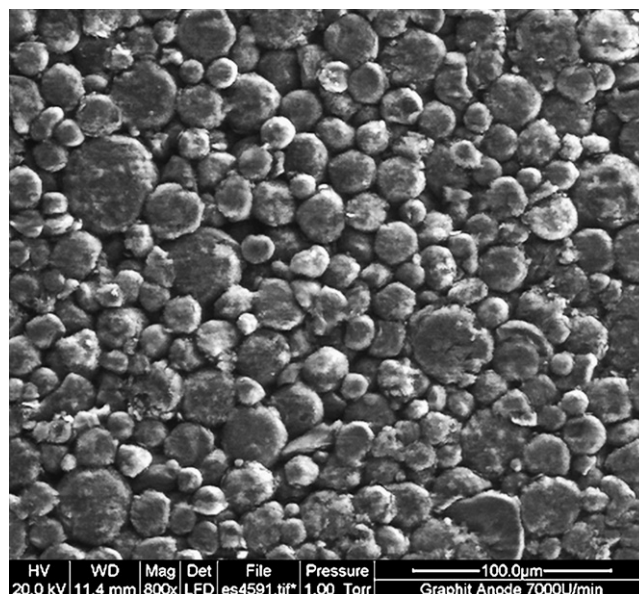


Fig. 4. The surface morphology of a pristine MCMB 1028 electrode.

investigated by comparing the aromatic BIC and the linear EtNCO with various analytical techniques.

3.2. Scanning electron microscopy (SEM)

Besides of formation voltage and chemical composition, also compactness and thickness of the SEI significantly affect performance. A “good” (i.e., compact, thin, etc.) SEI will lead to low self-discharge [11,19], low battery resistance and less polarization, thus further resulting in low capacity fading, high discharge capacity and long cycle life. Fig. 4 shows the SEM

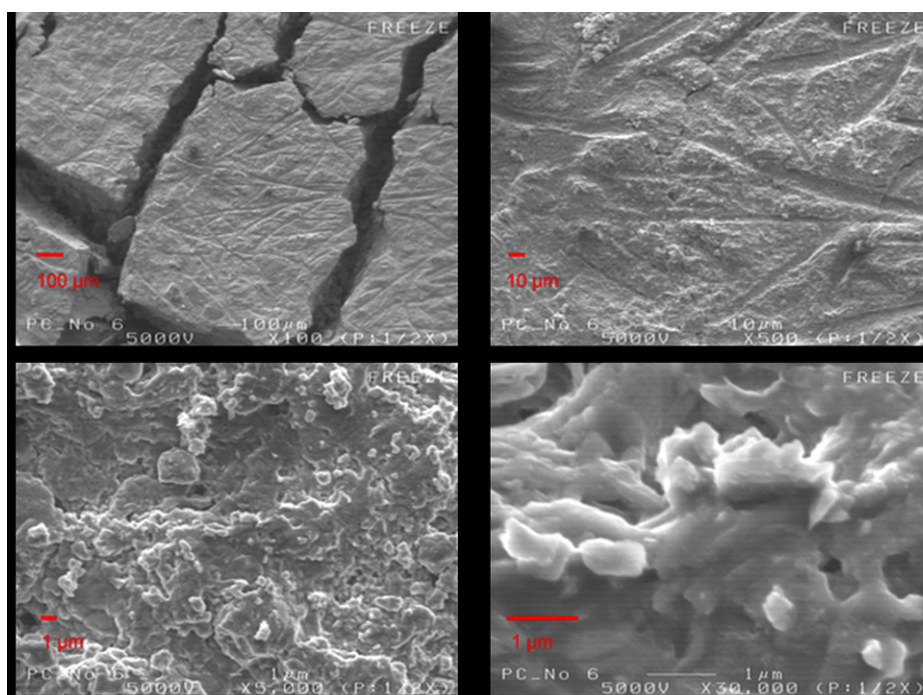


Fig. 5. The surface morphology of an MCMB electrode after SEI formation in 2 wt.% BIC in 1 M LiClO₄/PC at different magnifications.

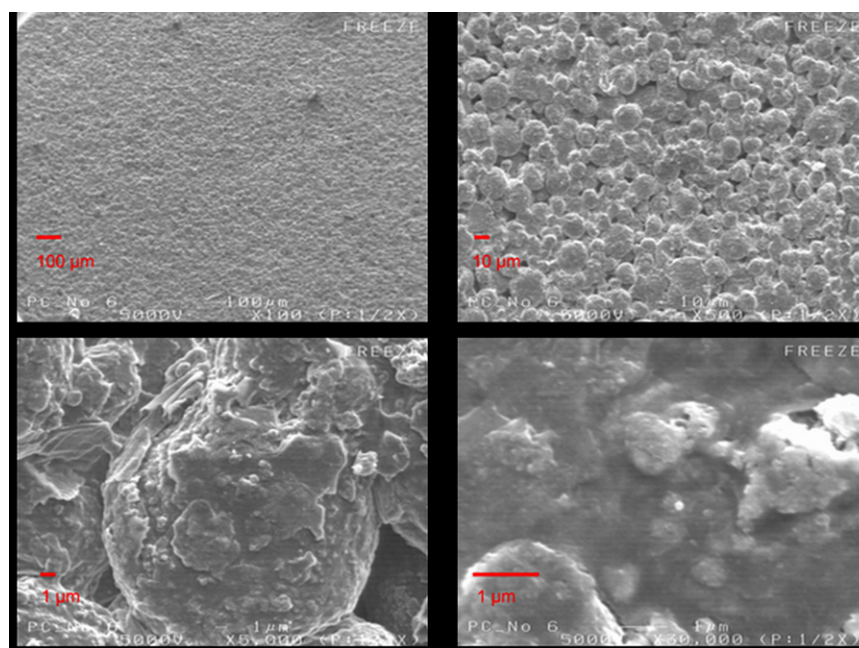


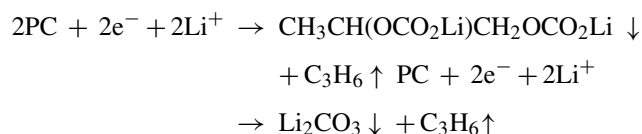
Fig. 6. The surface morphology of an MCMB electrode after SEI formation in 2 wt.% EtNCO in 1 M LiClO₄/PC.

of the pristine MCMB electrode. Graphite spheres with an average diameter of 25 μm are clearly visible. Fig. 5 shows the surface morphology of the negative electrodes after cyclic voltammetry (cf. Fig. 1) in the electrolyte: 2 wt.% BIC in 1 M LiClO₄/PC. The MCMB anode is covered by a thick layer of electrolyte decomposition products, indicating strong electrolyte decomposition. Furthermore, the electrode is strongly irreversibly expanded after the cyclic voltammetric experiment and contains cracks. The expansion indicates that processes such as co-intercalation and/or gassing have occurred. These observations are made despite the fact that BIC finally seems to work in a PC-based electrolyte. SEM images of the electrode cycled in 2 wt.% In EtNCO in 1 M LiClO₄/PC as electrolyte, the surface morphology stayed nearly the same as that of the pristine graphite (Fig. 6). The graphite spheres are however covered by a thin (!) layer of electrolyte decomposition product, which seems to fix the spheres to one another. No distinct dilatation can be observed.

3.3. On-line electrochemical mass spectrometry (on-line mS)

Solvent co-intercalation, gassing and related exfoliation reactions are the dominant reactions occurring during reduction of graphite in PC. With regard to gassing, mainly hydrogen and propylene gases are evolved [17,18,20,21,22].

Dey and Sullivan [20] and Aurbach et al. [23] proposed that the reductive decomposition of PC electrolytes proceeds according to



We have investigated the gassing behaviour of three different electrolytes versus MCMB 1028 graphite by on-line MS: 1 M LiClO₄ in PC with and without 10 wt.% of the additives BIC and EtNCO. For space reasons the results are not illustrated. Both, in the pure PC electrolyte and in the electrolyte with 10 wt.% BIC, propylene evolves when the anode potential decreases to ~900 mV versus Li/Li⁺.

This indicates PC decomposition due to solvated intercalation. Comparing the relative amount of propylene gas, BIC seems to diminish (but not fully avoid!) PC co-intercalation and subsequent gassing. With EtNCO in the electrolyte, propylene gas formation does not occur, indicating that PC co-intercalation is suppressed. These results are in line with the SEM data and electrochemical data. Strong reduction currents in the cyclic voltammogram indicate less effective SEI formation and thus a thicker SEI. The in parallel occurring PC co-intercalation reaction leads to propylene gassing and expanded electrodes.

3.4. In situ FTIR spectroscopy

IR bands characteristic for BIC have been monitored in situ to the electrochemical reduction of a GC electrode. The FTIR data obtained for EtNCO is discussed in a separate paper of this proceedings volume. Fig. 7 shows the IR spectra of 1 M LiClO₄/PC and of 10 vol.% BIC in 1 M LiClO₄/PC at a potential of 3 V versus Li/Li⁺. The molecule BIC comprises the isocyanate group represented by the IR band at ~2250 cm⁻¹ (asymmetric –NCO stretching vibration of isocyanates, indicated by *).

BIC reduction starts at potentials below ~1250 mV versus Li/Li⁺. To emphasize the changes of the characteristic IR band during this reduction in a more visible way, we took advantage of the SNIFTIRS method (Subtractively Normalized Interfacial FTIR Spectroscopy), i.e., the difference in transmission of the spectrum at a certain potential E_E is related to the reference

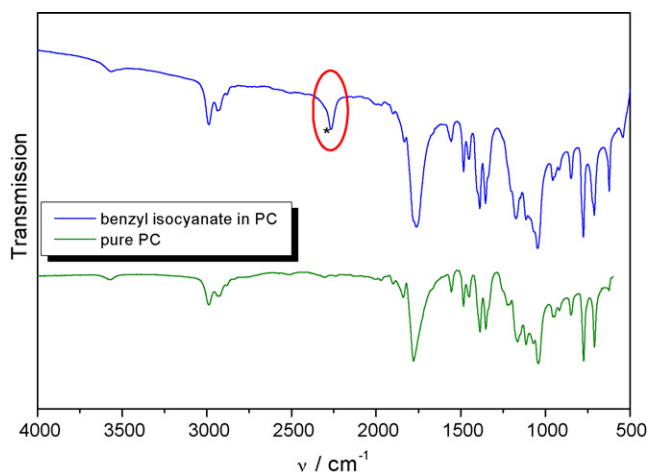


Fig. 7. Transmission FTIR spectra of 0.5 M LiClO₄/PC (below) and 10 vol.% BIC in 0.5 M LiClO₄/PC at glassy-carbon at open circuit potential.

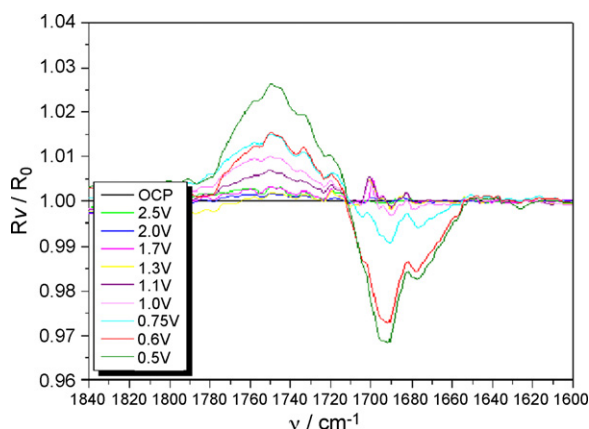


Fig. 8. SNIFTIR spectra of 10 vol.% BIC in 0.5 M LiClO₄/PC at a glassy-carbon electrode at different potentials vs. Li/Li⁺ (OCP to 0.5 V)—bands represent a decrease of the C=O stretching vibration of esters (1750 cm⁻¹) and an increase of the C=O stretching vibration of amides (1690 cm⁻¹).

spectrum R_0 taken at open circuit potential (OCP):

$$\frac{R_v - R_0}{R_0} = \frac{R}{R_0}$$

In the SNIFTIR spectrum a decrease in concentration of certain species is indicated by a positive band, an increase in concentration is expressed by a negative band. Figs. 8 and 9 show a decrease of the C=O stretching vibration of esters (1750 cm⁻¹) and an increase of C=O stretching vibration of amides (1690 cm⁻¹). The band at 2275 cm⁻¹ is representing a decrease of the asymmetric -NCO stretching vibration. This clearly confirms, that in the presence of BIC, reduction of the electrolyte is initiated by reaction of the -NCO function of the isocyanate compound. It might be assumed that the isocyanate monomer is converted into an intermediate radical anion according to the following reaction mechanism:

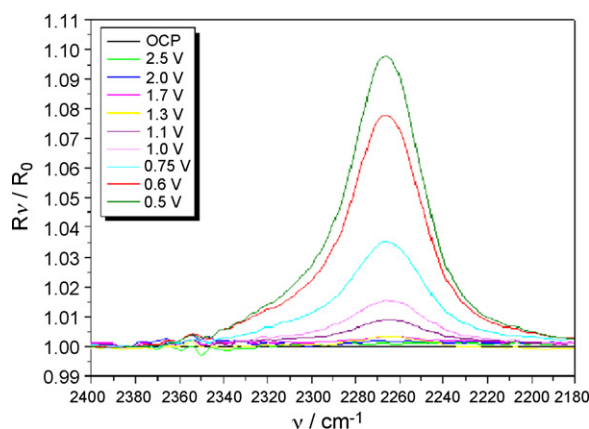
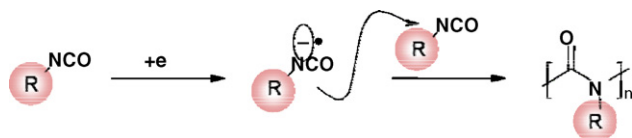


Fig. 9. SNIFTIR spectra of 10 vol.% BIC in 0.5 M LiClO₄/PC at glassy-carbon at different potentials vs. Li/Li⁺ (OCP to 0.5 V)—bands represent a decrease of the asymmetric -NCO stretching vibration (2275 cm⁻¹).

This intermediate may react with (i) other isocyanate monomers resulting into a polymer which participates in the SEI and (ii) with other electrolyte components (LiClO₄ or PC) resulting in mixed reduction and SEI products. These reactions might appear in parallel.

4. Conclusion

As like vinylene compounds, isocyanate compounds are an interesting family of SEI-forming electrolyte additives for lithium-ion batteries; and they also function according to an electrochemical polymerization mechanism. The final performance, however, strongly depends on the (i) chemical structure, (ii) steric similarities/differences, (iii) nature and position of potential electron withdrawing group(s), and (iv) the number and nature of heteroatoms within the molecule. The chances to identify new electrolyte additives via the search for compounds following a common-valid electrochemical operation mechanism are limited. The SEI formation behaviour can be predicted just to some extent. The final performance has to be examined with in situ and ex situ analytical and electrochemical tools compound by compound.

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