

## Ethyl isocyanate - An electrolyte additive for PC based electrolytes in lithium ion batteries

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The performance of graphitic carbons used as anodes in lithium-ion batteries depends on the presence of a film forming species, which is able to establish an electronically insulating and at the same time lithium-ion conducting SEI. In case of standard ethylene carbonate-based electrolytes, EC is responsible for this film 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 graphitic anodes due to co-intercalation and associated PC-decomposition [1,2]. The application of pure PC electrolytes requires the presence of a film forming species, i.e. a film forming electrolyte additive.

From early investigations in the field of preparative organic electrochemistry the reductive film-forming polymerization of isocyanates is well known [3,4]. Isocyanate compounds have been patented in various purposes for LIB's [5,6].

In this contribution we want to focus on ethyl isocyanate (EtNCO) which proved to perform well in PC electrolytes. The cyclic voltammogram of EtNCO (2 wt% in 1 M LiClO<sub>4</sub>/PC) illustrates that its reduction starts slightly below 1.2 V vs. Li/Li<sup>+</sup> (Fig. 1). Thereafter PC-decomposition is successfully avoided; the second cycle features a flat current curve in the filming potential area which indicates that the filming reaction is almost completed.

Charge cycling of graphite electrodes in an EtNCO-containing PC-electrolyte showed that this additive is able to efficiently protect graphite from exfoliation throughout cycling.

In order to get a deeper understanding of the way how EtNCO is reduced during the first charge, in-situ FTIR experiments were performed by using an institute made measuring cell. In order to use a carbon electrode with an IR reflecting surface a glassy carbon electrode was used as a model electrode for the commonly in lithium-ion cells used graphite. The investigation of dedicated infrared bands revealed that the reduction of EtNCO involves a reaction of the -NCO group. The results encourage a reduction mechanism for isocyanate compounds which proposes the formation of an intermediate radical anion (Fig. 2). The results of both, electrochemical and in-situ FTIR investigations will be comparatively discussed in this contribution.

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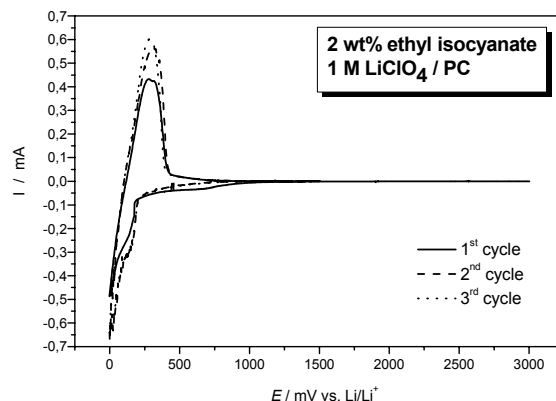


Figure 1: Cyclic voltammogram of a MCMB graphite electrode in EtNCO (2 wt%) in 1M LiClO<sub>4</sub>/PC; scan rate: 0.05 mV s<sup>-1</sup>.

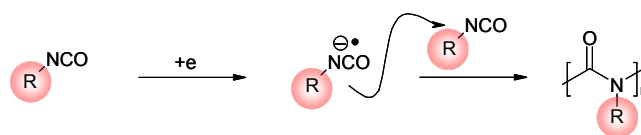


Figure 2: Cathodic reduction of isocyanates.

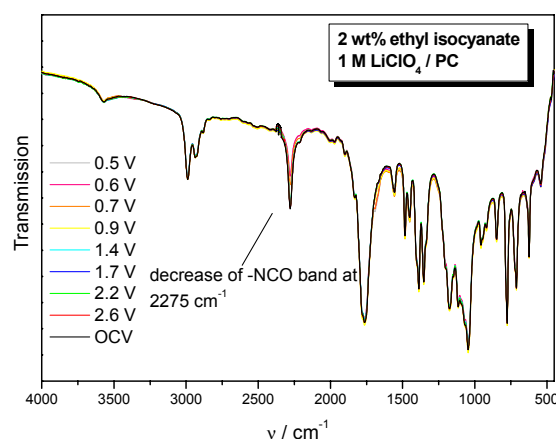


Figure 3: IR spectra of the electrolyte PC/ LiClO<sub>4</sub> at the glassy carbon electrode with 2 wt% EtNCO – decrease of asymmetric -NCO stretching vibration at 2275 cm<sup>-1</sup>.

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