

# In Situ ATR-FTIR Spectroscopic Investigations during Electrochemical Reduction of Fullerene Thin Films

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**Abstract.** Spectroelectrochemical investigations of the redox processes of C<sub>60</sub> fullerene films in Li<sup>+</sup> and TBA<sup>+</sup> containing electrolytes using *in situ* FTIR-ATR spectroscopy are shown. Using Li<sup>+</sup>, the reduction to C<sub>60</sub><sup>2-</sup>-salt and the reoxidation occur in two processes, whereas with TBA<sup>+</sup> only one reduction process and two less resolved reoxidation processes are observed.

## INTRODUCTION

Electrochemistry provides controlled conditions (defined redox potential, controllable amount of charge) for the redox processes of solid state fullerene films (1). Fourier transform infrared (FTIR) spectroscopy is a powerful tool to get information on structural and molecular properties of fullerenes. By combining the two methods in a special setup using cyclic voltammetry and attenuated total reflection (ATR) spectroscopy with germanium reflection elements as working electrodes (2), spectral information *in situ* during electrochemical redox processes of C<sub>60</sub> films in organic electrolytes is obtained.

## EXPERIMENTAL

The FTIR-ATR spectroelectrochemical setup and the method are described in (2). Working electrode: Pt covered Ge reflection element with a C<sub>60</sub> film, electrode area: 0.63 cm<sup>2</sup>, reference electrode: Ag/AgCl, counter electrode: Pt foil, electrolyte solution: 0.1 M lithium perchlorate (LiClO<sub>4</sub>) or tetrabutylammonium perchlorate (TBAClO<sub>4</sub>) in acetonitrile, temperature: -4 °C, scan rate: 5 mV/s, C<sub>60</sub> films (0.6 - 1 μm) prepared with hot wall beam epitaxy (HWBE), FTIR spectrometer: Bruker IFS66S. MCT-Detector, coadding of 32 interferograms for each spectrum, resolution: 4 cm<sup>-1</sup>. Each spectrum covers a range of about 90 mV in the cyclic voltammogram.

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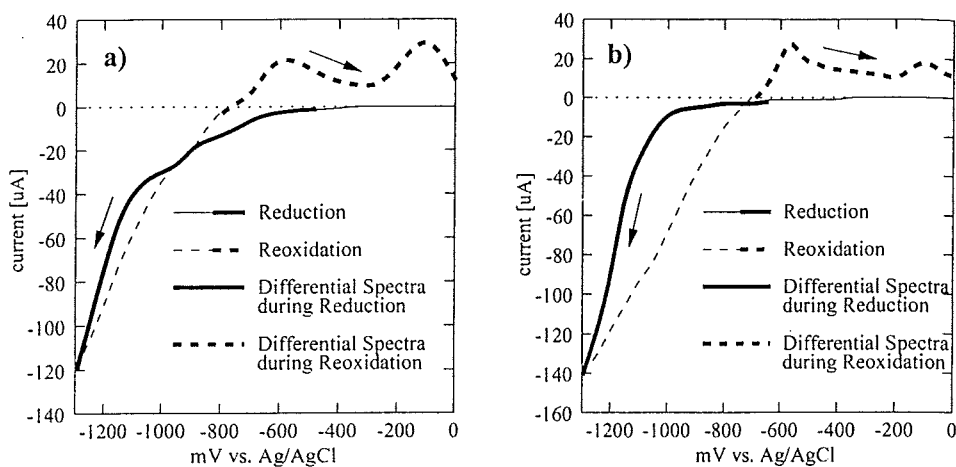


FIGURE 1: Cyclovoltammograms in a)  $\text{Li}^+$  and b)  $\text{TBA}^+$  containing electrolytes.

## RESULTS AND DISCUSSION

Figure 1 shows cyclovoltammograms of  $\text{C}_{60}$  films with  $\text{Li}^+$  and  $\text{TBA}^+$  containing electrolytes, which indicate a retarded reduction process, especially in presence of  $\text{TBA}^+$ . Similar behaviour has been observed by other authors during doping with  $\text{TBA}^+$  and has there been explained by film resistivity effects (1.3).

During reduction and reoxidation IR spectra were recorded consecutively. Differential spectra obtained by calculating each difference between two consecutive spectra are shown in Figure 2 for the reduction processes and in Figure 3 for the reoxidation processes in  $\text{Li}^+$  and  $\text{TBA}^+$  containing electrolytes. With differential spectra, the dynamic formation and consumption of substances can be seen by upwards and downwards pointing IR bands, respectively.

During reduction (Figure 2), a negative IR band at  $1428\text{ cm}^{-1}$ , attributed to a decreasing amount of  $\text{C}_{60}$  (4.5) on the electrode surface, is found in both electrolytes. Using  $\text{Li}^+$ , an upwards pointing band appears at  $1393\text{ cm}^{-1}$ , which upon further reduction shifts to  $1375\text{ cm}^{-1}$ . With  $\text{TBA}^+$ , the process is retarded and only at a later state of the reduction a band at  $1375\text{ cm}^{-1}$  can be seen. According to the literature (4.5), a band at  $1393\text{ cm}^{-1}$  can be assigned to the formation of  $\text{C}_{60}^-$ -salts. Since  $\text{C}_{60}^{3-}$  has been reported to show a band at  $1363\text{ cm}^{-1}$  (4,5), we attribute the band at  $1375\text{ cm}^{-1}$  to  $\text{C}_{60}^{2-}$ -salts. From the spectral data, the reduction of a  $\text{C}_{60}$  film in  $\text{Li}^+$  containing electrolyte shows two processes  $\text{C}_{60} \rightarrow \text{C}_{60}^- \rightarrow \text{C}_{60}^{2-}$  (partially overlapped), whereas with  $\text{TBA}^+$  the formation of the  $\text{C}_{60}^{2-}$ -salt occurs in one process  $\text{C}_{60} \rightarrow \text{C}_{60}^{2-}$ ; due to the more retarded reduction reaction.

In the  $1440\text{-}1470\text{ cm}^{-1}$  wavenumber range additional electrode potential dependent IR bands can be seen. A band at  $1467\text{ cm}^{-1}$  occurs predominately in the reaction  $\text{C}_{60} \rightarrow \text{C}_{60}^-$  (lower part in Figure 2a), and a band at  $1442\text{ cm}^{-1}$  in the

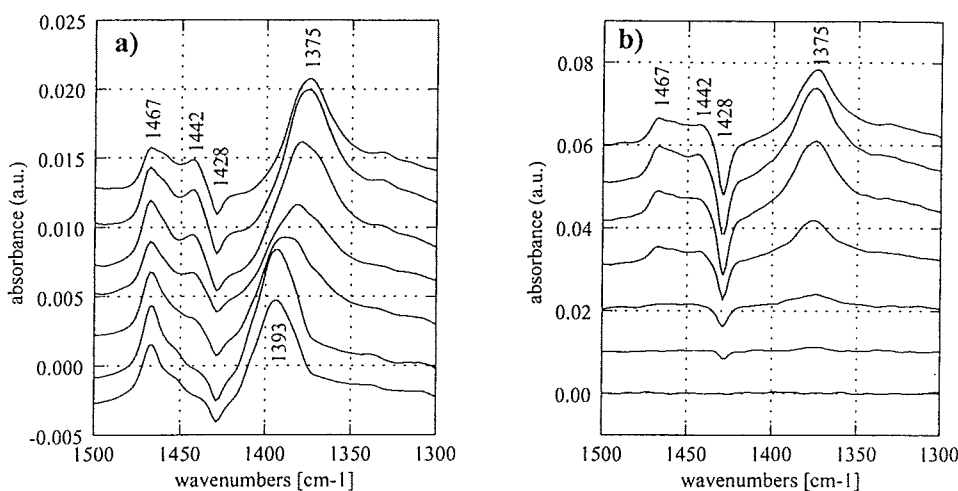


FIGURE 2: Differential spectra during reduction in a) Li<sup>+</sup> and b) TBA<sup>+</sup> containing electrolyte. The spectra are separated. Sequence: bottom to top.

reaction  $C_{60}^- \rightarrow C_{60}^{2-}$  (upper part in Figure 2a). The additional spectral features seen during reduction may be due to structural changes taking place in the film during doping (6) or the formation of dimers of  $C_{60}^{\bullet-}$  as proposed in (7,8).

In both electrolytes, the reoxidation processes occur in two steps around -600 and -100 mV/SCE (Figure 1). Comparing the differential spectra (Figure 3), the processes are better resolved in the case of Li<sup>+</sup>. At the more negative potential, a decreasing IR band at 1375 cm<sup>-1</sup> and an increasing band at 1393 cm<sup>-1</sup> (lower part in Figure 3a) indicate the oxidation of  $C_{60}^{2-}$ -salt to  $C_{60}^-$ -salt. Upon further reoxidation of  $C_{60}^-$  to  $C_{60}$  (upper part in Figure 3a) a decreasing IR band at 1393 cm<sup>-1</sup> and an increasing band at 1428 cm<sup>-1</sup> are obtained. Using TBA<sup>+</sup>, the processes are less resolved (Figure 3b). The intermediate  $C_{60}^-$ -salt can be seen by an increasing absorption at 1410 cm<sup>-1</sup> (lower part in Figure 3b) and a decreasing absorption around 1400 cm<sup>-1</sup> (upper part in Figure 3b). Morphological effects due to the larger size of the TBA<sup>+</sup> cation are probably responsible for the differences to the results using Li<sup>+</sup>.

The spectral features in the 1440-1470 cm<sup>-1</sup> wavenumber range during reoxidation occur in the reverse sequence compared to the reduction reaction. The band at 1442 cm<sup>-1</sup> vanishes in the reaction  $C_{60}^{2-} \rightarrow C_{60}^-$ , and the band at 1467 cm<sup>-1</sup> in the reaction  $C_{60}^- \rightarrow C_{60}$  (Figure 3a). Again, the effects are less resolved with TBA<sup>+</sup> (Figure 3b).

To summarize, FTIR ATR spectroelectrochemistry provides valuable information on the redox processes of  $C_{60}$  films. Comparing the results in Li<sup>+</sup> and TBA<sup>+</sup> containing electrolytes, Li<sup>+</sup> shows two reduction processes  $C_{60} \rightarrow C_{60}^-$ -salt  $\rightarrow C_{60}^{2-}$ -salt and two clearly separated reoxidation processes, whereas in the case of TBA<sup>+</sup> a

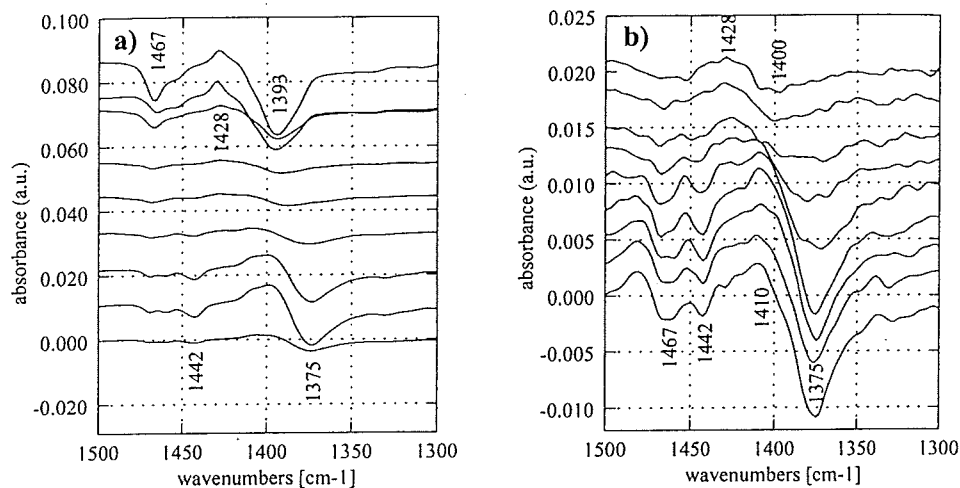


FIGURE 3: Differential spectra during reoxidation in a)  $\text{Li}^+$  and b)  $\text{TBA}^+$  containing electrolyte. The spectra are separated. Sequence: bottom to top.

more retarded reduction with a single process  $\text{C}_{60} \rightarrow \text{C}_{60}^{2-}$ -salt and poorly resolved reoxidation processes are observed.

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