

In situ ATR-FTIR spectroelectrochemical comparison of pristine and polymerized C₆₀ films

H. Neugebauer*, C. Kvarnström*[†], H. Sitter[‡], Ch. Jogl^{||}, H.
Kuzmany^{||} and N. S. Sariciftci*

*Physical Chemistry, Johannes Kepler University Linz, Altenbergerstraße 69, A-4040 Linz,
Austria

[†]Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland

[‡]Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz,
Altenbergerstraße 69, A-4040 Linz, Austria

^{||}Institute of Material Physics, University of Vienna, Strudlhofgasse 4, A-1090 Vienna, Austria

Abstract. In situ spectroelectrochemical studies on the reduction processes of solid fullerene films in different organic electrolyte solutions using cyclic voltammetry and attenuated total reflection (ATR) FTIR spectroscopy are presented. IR bands from the electrochemically induced reduction states of pristine and polymerized C₆₀ films are compared with spectra of the stable polymeric RbC₆₀ phase.

INTRODUCTION

In contrast to the electrochemistry of C₆₀ in solution, where up to six consecutive reversible one-electron reductions are obtained [1], the electrochemical behavior of solid fullerene films is more complicated [2]. The cyclic voltammetric response depends on the structure and the morphology as well as the composition of the electrolyte solution [3,4]. Especially the nature of the cation in the electrolyte was found to highly influence the reaction mechanisms and the reaction products [2].

In the present paper, in situ spectroelectrochemical measurements on the electrochemical reduction of C₆₀ films in different electrolyte solutions using a combination of cyclic voltammetry and attenuated total reflection (ATR) FTIR spectroscopy are presented. Since the formation of dimeric [5] and polymeric phases during electrochemical reduction have been proposed, the spectra are compared with spectra of polymeric forms of C₆₀ (photopolymerized C₆₀ and the stable polymeric RbC₆₀ phase, for an overview of the polymeric forms of C₆₀ see e.g. [6]).

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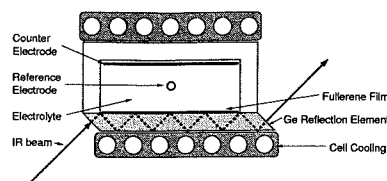


FIGURE 1. Spectroelectrochemical cell for *in situ* ATR-FTIR spectroscopy with Ag/AgCl reference electrode and Pt counter electrode.

EXPERIMENTAL

C_{60} films were prepared by solution casting or by hot wall beam epitaxy (HWBE) [7] on the surface of Pt covered Ge reflection elements used for ATR-FTIR spectroelectrochemistry (Fig. 1, for details of the method see [8]). Photopolymerization of C_{60} was done by illumination of the film with UV light under vacuum. The polymeric form of RbC_{60} was prepared by exposure to Rb vapor at 450 K and slowly cooling to room temperature. Electrolyte solutions were 0.1 M TBAClO₄ (TBA = tetrabutylammonium), TBABF₄, LiClO₄, KPF₆, NaBF₄ and 0.01 M (due to the low solubility) RbBPh₄ (Ph = phenyl) in acetonitrile. During slow reductive potential scans FTIR spectra were recorded consecutively with a Bruker IFS66S spectrometer (MCT detector, resolution 4 cm⁻¹). For each spectrum 32 interferograms were coadded, which covers a range of about 90 mV in the cyclic voltammogram.

RESULTS AND DISCUSSION

Figure 2 shows difference spectra during the reduction processes of fullerene films in different electrolytes. Besides Rb⁺, all experiments were done with HWBE films. With Rb⁺, no electrochemical response was obtained with HWBE films, probably due to the low electrolyte concentration (low solubility of RbBPh₄). The spectra with Rb⁺ were measured with a solution casted film. The resulting spectra were analyzed in respect to the frequency of the $F_{1u}(\omega_4)$ mode of C_{60} (characteristic for the amount of charge on C_{60} [6,9]) during reduction with different cations as follows: for TBA⁺ (Fig. 2a): band at 1375 cm⁻¹, formation of C_{60}^{2-} in one step [3]; for Li⁺ (Fig. 2b): a band at 1393 cm⁻¹ evolves and shifts to 1382 cm⁻¹, two step reduction $C_{60} \rightarrow C_{60}^- \rightarrow C_{60}^{2-}$ [3]; for Na⁺ (Fig. 2c): band at 1394 cm⁻¹, formation of C_{60}^- ; for K⁺ (Fig. 2d): more complicated structure, a band at 1375 cm⁻¹ is attributed to C_{60}^{2-} , but the shoulder at lower wavenumbers indicates also the formation of higher reduction states; for Rb⁺ (Fig. 2e): the broad pattern around 1365 cm⁻¹ indicates mainly the formation of C_{60}^{3-} in dropcasted C_{60} films, in contrast to photopolymerized C_{60} , Rb⁺ (Fig. 2f): band at 1396 cm⁻¹ attributed to the formation of C_{60}^- .

For comparison, the ATR spectra of polymeric forms are shown in Fig. 3. As

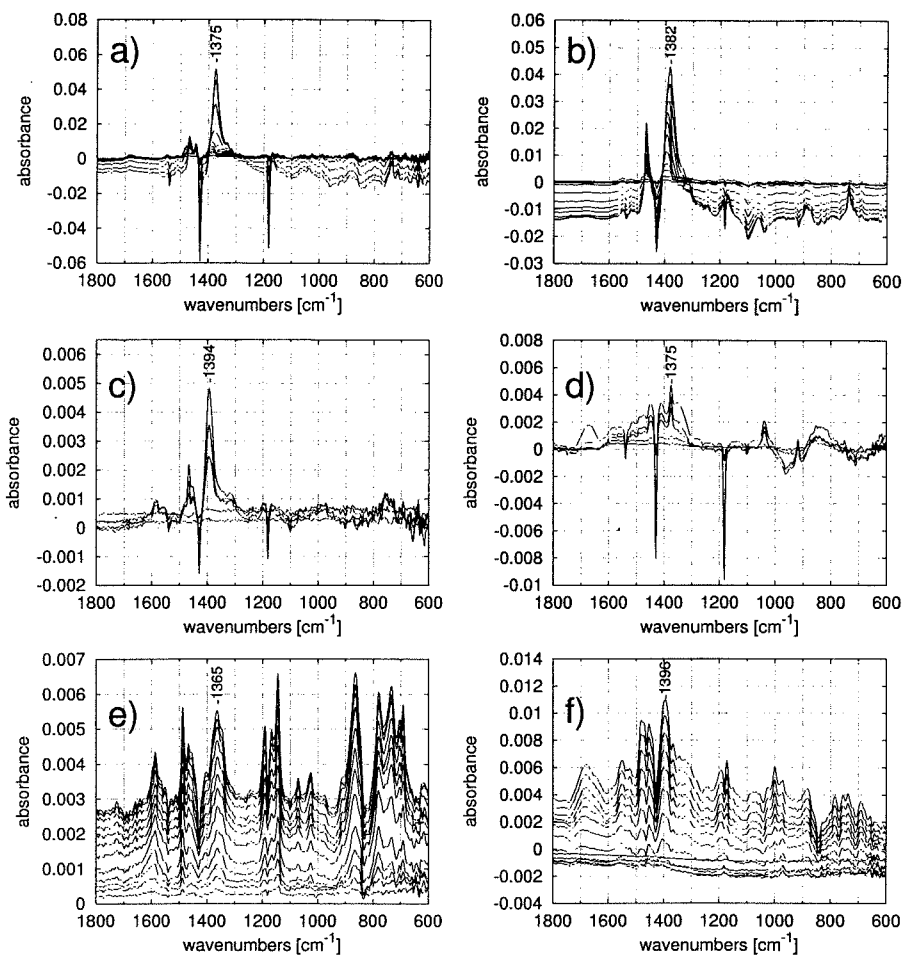


FIGURE 2. Difference spectra during reduction of C_{60} films in different electrolytes, reference spectrum: neutral form. a) HWBE C_{60} film in 0.1 M $TBAClO_4$, b) HWBE C_{60} film in 0.1 M $LiClO_4$, c) HWBE C_{60} film in 0.1 M $NaBF_4$, d) HWBE C_{60} film in 0.1 M KPF_6 , e) drop casted C_{60} film in 0.01 M $RbBPh_4$, f) photopolymerized HWBE C_{60} film in 0.01 M $RbBPh_4$.

can be seen, the reduction of C_{60} and of photopolymerized C_{60} in Rb^+ containing electrolyte does not result in the polymeric RbC_{60} structure obtained by vapor doping (Fig. 3a).

A spectral feature around 1460 cm^{-1} was found for photopolymerized C_{60} [6] (Fig. 3b) as well as for C_{60} dimers [10]. Bands in this spectral region are also observed during electrochemical reduction of C_{60} films in all electrolyte solutions used (Fig. 2).

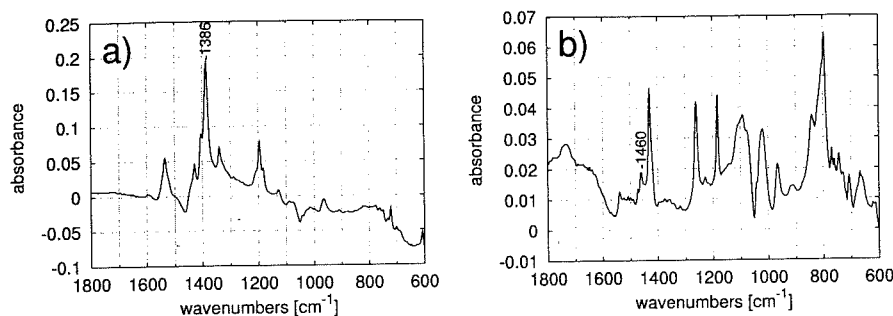


FIGURE 3. ATR spectra of polymeric forms. a) RbC₆₀. b) Photopolymerized C₆₀.

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