

Investigations of fullerene thin films with in situ FTIR spectroelectrochemistry

C. Kvarnström^{a,b}, H. Neugebauer^a, G. Matt^a, H. Sitter^c, N.S. Sariciftci^a
^aPhysical Chemistry, Johannes Kepler University Linz, A-4040 Linz, Austria
^bAnalytical Chemistry Åbo Akademi University, FIN-20500 Åbo-Turku, Finland
^cInst. Semiconductor Physics, Johannes Kepler University Linz, A-4040 Linz, Austria

Abstract

In situ internal reflection FTIR spectroscopy measurements using the attenuated total reflection (ATR) method were made during electrochemical reduction of fullerene films. Thin C₆₀ films were prepared either by solution casting from a fullerene-CH₂Cl₂ solution or by molecular beam epitaxy technique. The spectroscopic characterization of the film structure was made for the different redox processes in organic electrolyte media during potential cycling in a temperature controlled spectroelectrochemical cell using a Ge crystal as working electrode. The IR spectra obtained during the redox processes of the fullerene films in different electrolyte solutions are discussed.

Keywords: In situ electrochemical spectroscopy, electrochemical doping, infrared spectroscopy, fullerenes, thin films

1. Introduction

The infrared spectrum of C₆₀ contains four strong intramolecular modes F_{1u} at $\omega_1=526$, $\omega_2=576$, $\omega_3=1182$ and $\omega_4=1428$ cm⁻¹ [1]. Three of the modes, ω_1 , ω_2 , ω_4 show doping induced shifts when solid C₆₀ is doped [2]. FTIR studies on chemical alkali metal doping of C₆₀ showed that the shift of the IR modes due to doping correlates with the number of electrons transferred to the C₆₀ molecule and is barely dependent on the nature of the dopant [3]. Electrochemistry facilitates the study of the different redox steps in the doping of C₆₀ films under controlled conditions. In this work cyclic voltammetry (CV) has been used for electrochemical doping of C₆₀ simultaneously as FTIR spectra were recorded in situ using the attenuated total reflection (ATR) technique.

2. Experimental

Films of C₆₀ were made by solution casting or by hot wall beam epitaxy (hwbe) growth with film thickness of 200–1000 nm. The electrochemical doping was made in a temperature controlled spectroelectrochemical three-electrode cell. The ATR-FTIR setup has been described elsewhere [4]. A germanium reflection element was used as working electrode (A = 0.63 cm²), Ag/AgCl as reference and a Pt foil as counter electrode. Freshly distilled acetonitrile (Aldrich) was used as solvent. Electrolyte solutions were 0.1 M TBAClO₄ (TBA=tetrabutylammonium), LiClO₄, KPF₆, NaBF₄ and 0.01 M RbBPh₄. Electrochemistry was controlled by a Jaissle potentiostat and the spectra were recorded by a Bruker IFS66S FTIR spectrometer with a MCT detector. For each spectrum 32 interferograms were coadded, which covers a range of approximately 60 mV in the cyclic voltammogram.

3. Results and Discussion

The cyclic voltammetric response of the reduction of a C₆₀ film is highly dependent on experimental parameters, like scan rate and temperature, which has been explained by competing chemical reactions (e.g. dimerization) parallel to the electrochemical

reaction [5]. Also the morphology and the structure of the film influences the CV response as can be seen in Figure 1a, where the first cycle of a C₆₀ film made by the hwbe technique and of a solution cast film are shown. Due to the compact crystalline structure of the hwbe film, its electrochemical doping reaction is retarded and the redox processes are less resolved compared to the solution cast film.

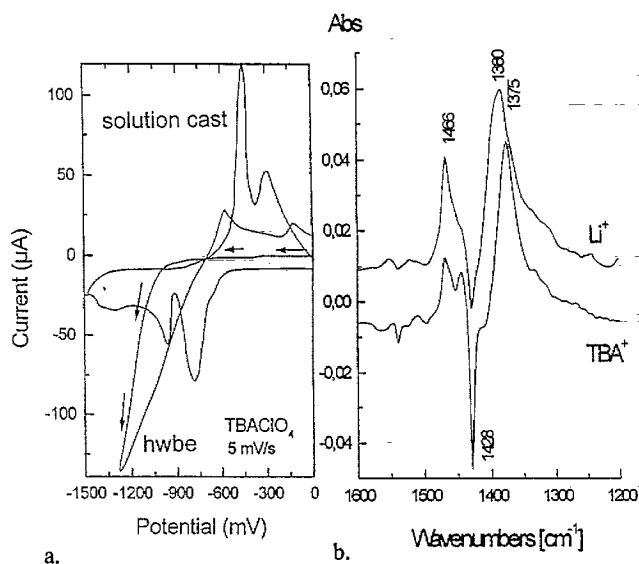


Figure 1a. CV of a hwbe grown C₆₀ film compared to a solution cast film, 0.1 M TBAClO₄-acetonitrile solution, scan rate 5 mV/s, T = 0 °C. **1b.** Difference FTIR spectra during the reduction of hwbe C₆₀ films in TBAClO₄ and in LiClO₄. Spectra shown are from the 2nd cycle in the range -1110 to -1170 mV, reference spectrum at -400 mV.

In Figure 1b, in situ FTIR difference spectra during electrochemical reduction of C_{60} hwbe films in the range -1110 mV to -1170 mV in presence of TBA^+ and Li^+ are shown. With TBA^+ , the decrease of the band at 1428 cm^{-1} and the increase of the band at 1375 cm^{-1} ($F_{1u}(4)$ mode) occur simultaneously, indicating that C_{60}^{2-} is formed in one step [6]. As has been shown in a previous paper [6] the electrochemical reduction of C_{60} is slightly more resolved in presence of Li^+ . The band at 1428 cm^{-1} changes in two steps first to 1393 cm^{-1} and further to 1380 cm^{-1} , which is explained by a two step reduction $C_{60} \rightarrow C_{60}^-$ and $C_{60}^- \rightarrow C_{60}^{2-}$ [6].

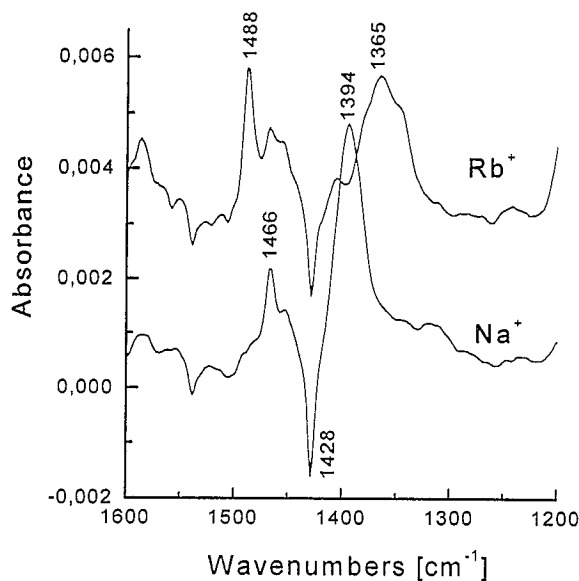


Figure 2. Difference spectra during reduction of C_{60} films. Upper spectrum: solution cast film in (0.01 M) $RbBPh_4$ -acetonitrile solution. Lower spectrum: hwbe film in (0.1M) $NaBF_4$ -acetonitrile solution. The spectra cover the range -1140 to -1200 mV, reference spectra at -400 mV.

Alkali metal doping of C_{60} films has been reported to proceed differently depending on the alkali metal used [7]. The difference in the size of the doping cation influences the structure of the doped C_{60} film. Smaller cations like Na^+ penetrate the C_{60} structure more easily than bigger cations like Rb^+ . Due to steric strains in the film caused by the dopant the solid can either keep the face centered cubic structure of the pristine crystal or transform to a body centered cubic or body centered tetragonal structure [7].

The cyclic voltammetric behaviour of hwbe grown and solution cast C_{60} films in presence of alkali cations is similar to the cyclic voltammograms shown in Fig. 1a. However, in the case of Rb^+ no redox reaction occurred in the case of hwbe films, probably due to the low concentration of the electrolyte salt (low solubility in acetonitrile) in combination with the compact crystalline structure of the hwbe film. However, with solution cast films the redox reactions were observed also in 0.01 M $RbBPh_4$ -acetonitrile electrolyte.

In situ FTIR difference spectra during electrochemical doping of C_{60} films in presence of Na^+ (hwbe film) and Rb^+ (solution cast film) are shown in Fig. 2. With Rb^+ , a broad peak at 1365 cm^{-1} is formed upon reduction. The peak starts to develop from the beginning of the reduction at -700 mV simultaneously as a negative peak from C_{60} at 1428 cm^{-1} occur. A peak at 1365 cm^{-1} has been assigned in the literature to C_{60}^{3-} salts [2]. The results indicate an electrochemical conversion of C_{60} into a trivalent reduced state. The stable polymeric form of RbC_{60} obtained by vacuum doping [2] is not formed by electrochemical doping.

Doping with Na^+ is known to be different from the other alkali metals due to the smaller ionic radius causing different structural phenomena [7]. The most stable reduction state of C_{60} in the $Na-C_{60}$ system is reported to be C_{60}^{2-} . However, in the spectra during electrochemical reduction in presence of Na^+ a peak at 1394 cm^{-1} occurs and remains unchanged even when applying higher negative potentials. This peak has been assigned in the literature to C_{60}^- structures [2]. Additional FTIR bands arising during reduction can be seen in the region $1450-1500\text{ cm}^{-1}$. A reversible band at 1466 cm^{-1} occurs independently on the doping cation. With Rb^+ an additional band at 1488 cm^{-1} can be seen. Bands in this region have been assigned to structural changes in the material taking place during reduction.

The FTIR spectroscopic comparison of the reduction states obtained by electrochemical doping especially with respect to structural effect (e.g. dimerization, polymerization) are subject of further investigations.

4. References

1. W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* 347 (1990) 354.
2. H. Kuzmany, M. Matus, T. Pichler and J. Winter. In K. Prassides (ed.) *Physics and Chemistry of Fullerenes*, Kluwer, Academic Press, Dordrecht. NATO ASI-C Series: Crete. Vol. 443 (1993) 287.
3. M. S. Dresselhaus, G. Dresselhaus and P.C. Eklund, *Science of fullerenes and carbon nanotubes*, Academic Press, Inc. 1995 San Diego, p. 382.
4. H. Neugebauer and Z. Ping, *Mikrochim. Acta [Suppl.]* 14 (1997) 125.
5. J. Heinze and A. Smie in *Recent advances in the chemistry and physics of fullerenes and related materials*, (ed.) K.M. Kadish and R.S. Ruoff, *Proceedings Volume 94-24*, (1994) The Electrochemical Society, Inc, p.1117.
6. H. Neugebauer, C. Kvarnström and N.S. Sariciftci, *Proceedings IWEPNM98 Kirchberg 1998*, in press.
7. D. W. Murphy, M.J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbagh, J. C. Tully and R. E. Walstedt, *J. Phys. Chem. Solids*, 53 (1992) 1321.

5. Acknowledgements

This work was supported by the „Fonds zur Förderung der wissenschaftlichen Forschung“ of Austria (Project No. P11457-CHE). C. K. thanks the Research Institute of the Foundation of Åbo Akademi University for scholarship.