Electrochemical Synthesis of Polymerized LiC$_{60}$ Films

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Electrochemical reduction of a C$_{60}$ solution (acetonitrile/toluene) in the presence of LiClO$_4$ on a Pt working electrode at elevated temperatures led to the formation of insoluble, reddish-brown carbon films. Various spectroscopic analyses (Raman, time-of-flight mass, FT-IR, NMR) revealed the presence of a negatively charged, polymeric phase of intact C$_{60}$ moieties interspersed with Li$^+$ counterions. SEM analysis showed the growth of highly disordered spherical particles of several micrometers in size. Semiempirical MO calculations of the models of initial dimerization process of monomer radical anions support the assumption of a spontaneous radical polymerization process.

1. Introduction

Recent years have witnessed a growing interest in the investigation of synthetic routes to and properties of C$_{60}$ in the polymerized state. Several different methods have been established to transform molecular C$_{60}$ into all-carbon polymers: photopolymerization,[1] plasma polymerization,[2] pressure-induced polymerization,[3] and alkali metal doping of C$_{60}$.[4] The latter, electron-induced synthesis was shown to yield conductive linear chains of polymerized C$_{60}$.[4−6]

Electrochemical studies of C$_{60}$ often focused on the short-term voltammetry of molecular C$_{60}$ film electrodes[7−10] rather than on the long-term bulk electrolysis of C$_{60}$ solutions.[11−13] The formation and characterization of cathodic organic films have been reported after bulk electrolysis of oxygenated fullerene materials.[14,15]

The present study introduces an electrochemical synthetic method to polymerized C$_{60}$ materials intercalated with Li cations by means of the cathodic electroreduction of C$_{60}$ in the absence of oxygen. The thin films were spectroscopically characterized by laser desorption−ionization time-of-flight mass spectrometry (LDITOF-MS), FT-IR, Raman, energy dispersive X-ray analysis (EDX), ^{13}C NMR, ^{7}Li NMR, and SEM investigation. Semiempirical molecular orbital calculations provide further insight in favor of a spontaneous polymerization process leading to the electrochemical film formation.

2. Experimental Section

2.1. Electrochemical Synthesis. A conventional electrochemical three-electrode cell was used for preparation of the all-carbon thin films. Special care was taken to operate the cell under oxygen-free conditions. A Pt plate and a Pt wire served as working and counter electrode, respectively. A Ag wire was used as reference electrode. The solvent consisting of a 1:3 v/v mixture of acetonitrile and toluene was used in the preparation of the films. Acetonitrile and toluene were dried over

molecular sieve and sodium/potassium (1:1) alloy, respectively, and transferred into the cell by vacuum sublimation. In the solvent 0.1 mM C$_{60}$ powder and well-dried 0.1 M LiClO$_4$ were dissolved. The C$_{60}$ powder was prepared and purified according to the procedure reported previously.[16] The cell was kept under nitrogen at all times to ensure the absence of dioxygen during the entire synthetic procedure. The cell was finally heated to 50 °C in an oil bath under magnetic stirring (1000 rpm) to enhance convective mass transport during the electrochemical transformations.

The cyclic voltammetric behavior of the dissolved C$_{60}$ was measured using a potentiostat/galvanostat HA-305 HD from Hokuto Denko Ltd. Then, the power source was switched into the galvanostatic mode to obtain a constant rate of charge transfer, and correspondingly, a constant rate of film formation although similar results were also obtained under potentiostatic conditions. The initial reduction current ($-100 \, \mu$A) was chosen such that the measured cell potential was slightly negative of the potential of the first reduction wave of C$_{60}$ (-0.9 to -1.0 V vs Ag). In the course of the galvanostatic reduction process, the total current was adjusted to keep the potential within the desired range. After a reaction time of $10-14$ h, deposition of a red-brown film was observed on the working Pt cathode. Prior to spectroscopic measurements the film was thoroughly rinsed with dried acetonitrile and toluene in order to remove remaining monomeric C$_{60}$ and salts (LiC$_{60}$, Li$_2$C$_{60}$). Finally, the film was dried for several hours under ultrahigh-vacuum conditions to remove the remaining solvent without heating.

2.2. Spectroscopic Measurements. All samples of electrochemically transformed films were stored under nitrogen and rapidly transferred for spectroscopic measurements.

LDITOF-MS was performed using a Thermo Quest Vision 2000 reflectron type mass monitor equipped with a N$_2$ laser. A Nicolet Magna 550 II spectrometer was used for recording the IR spectra in reflectance mode under a nitrogen atmosphere. Raman spectra were obtained at low (<15 mW/mm^2) excitation laser power to avoid phototransformation of the carbon films. An Ar$^+$ laser (514.5 nm) was used for excitation. The SEM was a Hitachi S-800 model. Prior to observation, the samples were sputter-coated with a thin film of Au. ^{7}Li and ^{13}C solid-

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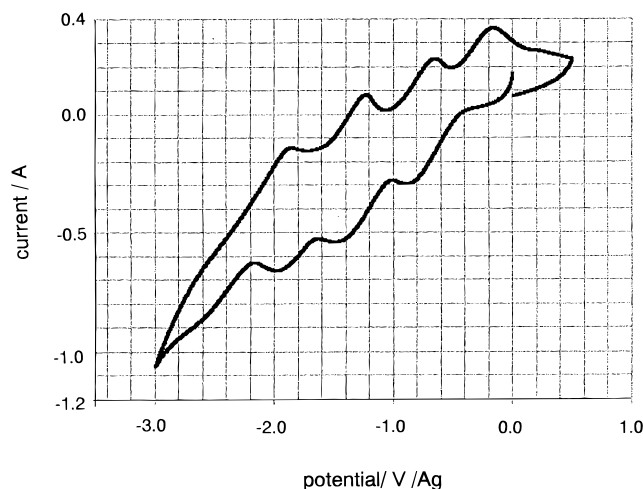
Figure 1. Cyclic voltammogram of C_{60} (0.1 mM) dissolved in an acetonitrile:toluene (1:3 v/v) solution containing 0.1 M $LiClO_4$ as supporting electrolyte.

state nuclear magnetic resonance (NMR) observations were performed using a JEOL GSX-270 NMR system. Single-pulse excitation mode was used for both nuclei under magic-angle spinning at 5000 rpm.

2.3. Calculations. The initial dimerization process of monomeric LiC_{60} was examined with a semiempirical MOPAC method[17] utilizing a MNDO Hamiltonian.[18] Symmetry constraints were not included for the geometry optimization procedure, and the SCF convergence criteria were set at 10^{-8} kcal/mol. Calculations were performed using the CAChe system (SONY Tektronix) coupled to a Mulliken system (IBM).

3. Results and Discussion

3.1. Film Preparation and Structural Analysis. Figure 1 shows the initial voltammetric profile of a C_{60} solution under the aforementioned conditions at small negative overpotentials. Clearly visible is the first reversible reduction wave at −0.8 V/Ag, corresponding to the C_{60}/C_{60}^- redox couple and to the formation of monomeric LiC_{60}. Unlike voltammetric profiles measured in the presence of large anions of the supporting electrolyte such as TBA^+ or Rb^+,[14,15] no further reduction wave was observed, but solvent decomposition started at potentials beyond −1.5 V/Ag. Galvanostatic electrolysis resulted in the deposition of a reddish-brown film which was insoluble in toluene and acetonitrile. These findings rule out the presence of intact C_{60} and monomeric fullerite salts such as LiC_{60} or Li_2C_{60} which are highly soluble in acetonitrile.[7] The films are stable under exposure to ambient atmosphere. It is important to note that the synthetic conditions are distinct from those reported to lead to a $C_{60}O$ polymer film by electrochemical reduction of C_{60} in the presence of oxygen.

Figure 2 shows two SEM images of the surface morphology of the cathodically grown film. Both parts a and b of Figure 2 show highly disordered spherical units of up to several micrometers in diameter with wide size distribution noticeable in Figure 2b. The morphology is distinct from the dual growth morphology found in polymeric C_{60} formed in the presence of oxygen.[15] The EDX analysis revealed a dominant C peak, with trace quantities of Cl and O.

The LDITOF MS of the electrochemically prepared film was observed at laser powers that were verified never to cause photoinduced polymerization of evaporated C_{60} film on the ionization target. The strong peak at $m/z = 720$ confirms that the intact cage of C_{60} was maintained in the electrochemically
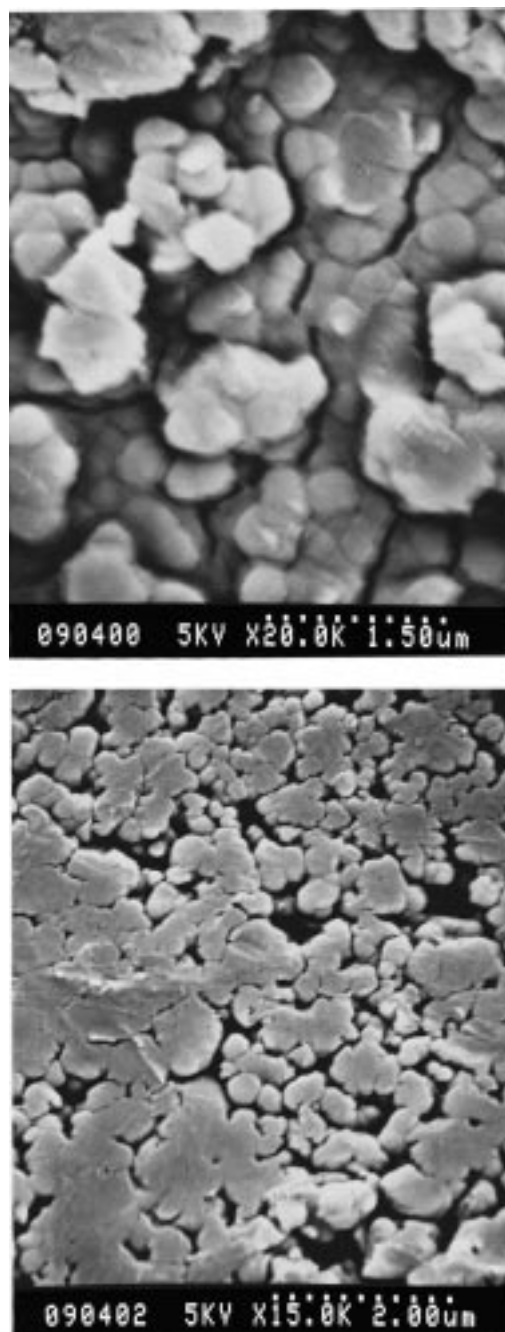

Figure 2. SEM images of the surface morphology of the electrochemical film: (a, top) scale = 1.5 μm, (b, bottom) scale = 2 μm.

prepared film. A smaller peak at $m/z = 696$ furthermore suggests the loss of C_2 upon laser desorption in the course of mass observation. No notable peak could be observed in the dimeric region. This feature compares well to a recent study[19] where the direct laser desorption of the pure dimeric C_{120} species could not be achieved due to the ready dissociation of C_{120} into monomeric C_{60} and C_{60-2n} fragments upon irradiation.

In the FTIR spectrum, the presence of intact C_{60} and the solvent molecules can be ruled out due to the absence of their absorption lines. Instead, a number of new broad lines at 866, 1087, 1433, 1494, and 1601 cm^{-1} are apparent. Similar broad IR vibrations were reported in the pressure-polymerized C_{60}[20,21] and in the electrochemically transformed $C_{60}O$.[15] It is unclear whether the most prominent peak at 1433 cm^{-1} is due to a molecular C_{60} (1424 cm^{-1}) upon polymerization. Although a
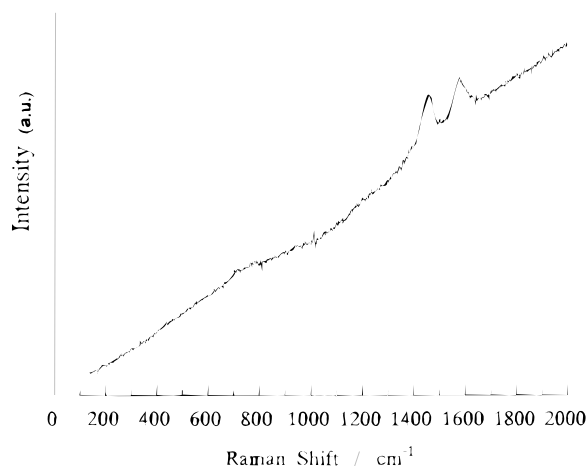
Figure 3. Room-temperature Raman spectrum of the electrochemical film at a low incident laser power (<15 mW/mm^2).
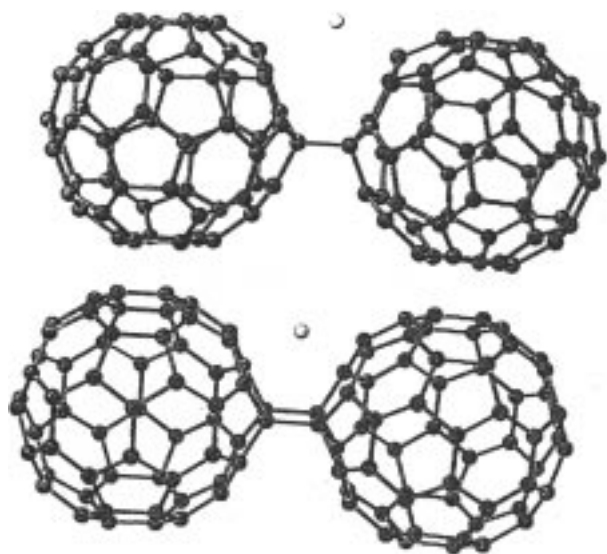

Figure 4. Optimized structures of the relevant dimers species involved in the initial dimerization process of C$_{60}^-$Li$^+$: (a, top) (C$_{60}$—C$_{60}$)$^-$Li$^+$ diradical intermediate formed by addition of C$_{60}^-$Li$^+$ and C$_{60}$; (b, bottom) C$_{120}^-$Li$^+$ dimer with cyclobutane structure.

TABLE 1: Calculated Heats of Formation ΔH_f^o (kcal/mol) of Species and Intermediates Potentially Involved in the Initial Dimerization Processes[a]

species	ΔH_f^o	species	ΔH_f^o
C$_{60}$	869.4	C$_{120}^-$Li$^+$ (b)	1513.8
C$_{60}^-$Li$^+$	763.0	(C$_{60}$—C$_{60}$)$^{2-}$(Li$^+$)$_2$	1595.0
(C$_{60}$—C$_{60}$)$^-$Li$^+$ (a)	1546.7	C$_{120}^{2-}$(Li$^+$)$_2$	1468.3

[a] Small letters in parentheses refer to the corresponding structures shown in Figure 4.

To clarify the chemical structure of the film, ^{7}Li and ^{13}C solid-state NMR were taken. In the ^{7}Li NMR spectrum, a single peak was observed at −256 ppm from the metallic Li line. This shift coincided with the Knight shift of LiCl, indicating that Li exists in the film in the ionic state. The free induction decay of ^{13}C nuclear magnetization showed that the transverse relaxation time (T_2) is in the range of microseconds. Despite proper application of the window function for Fourier transformation, the resulting spectrum contained uncertainties in frequency and line width. Since the film does not include metallic Li having electronic paramagnetism, the very rapid T_2 decay of ^{13}C nuclear magnetization was attributed to the strong spin dipolar perturbation effect by unpaired electrons migrating within the polymer. These NMR findings suggest that the formation of Li$^+$C$_{60}^-$ is the initial mechanistic stage toward the growth of insoluble and polymeric C$_{60}$ materials at the cathode and that Li exists in the cationic state forming ion pairs with reduced C$_{60}$ polymeric units.

3.2. Formation Dynamics. Although we have not observed definitive evidence of intermolecular cross-linking, the spectroscopic results strongly suggest the polymer formation of C$_{60}$. Hereafter, the structure and process of polymerization of C$_{60}$ are examined using semiempirical calculations including Li. The calculated values of heat of formation (ΔH_f^o) of the relevant species are shown in Table 1, and the corresponding optimized dimer structures are shown in Figure 4. At the first ionization potential, C$_{60}$ is reduced to the C$_{60}^-$ ion which undergoes immediate transformation into a C$_{60}^-$Li$^+$ radical ion pair. For the ion pair, the calculations suggest that the Li$^+$ is located on top of a hexagon with the unpaired electron being concentrated in the hexagon facing toward the Li$^+$. The heat of reaction (ΔH_f^o(r)) in the formation of the radical ion pair was found to be −106.42 kcal/mol, indicating an exothermic process. As is well-known, C$_{60}$ reacts quickly with organic radicals.[26] Hence, the formation of an ion pair is likely to be followed by the addition to molecular C$_{60}$, yielding an intermediate (C$_{60}$—C$_{60}$)$^-$-Li$^+$ having a single pivot C—C bond as shown in Figure 4a. Since the (C$_{60}$—C$_{60}$)$^-$Li$^+$ species has two open-shell carbons around the pivot bonds, the intermediate should undergo spontaneous transformation into the C$_{120}^-$Li$^+$ species having a cyclobutane structure as depicted in Figure 4b. Indeed, ΔH_f^o(r) in the formation of (C$_{60}$—C$_{60}$)$^-$Li$^+$ from C$_{60}$ and (C$_{60}$)$^-$Li$^+$ was calculated to be −85.74 kcal/mol, and the C$_{120}^-$Li$^+$ was more stable than (C$_{60}$—C$_{60}$)$^-$Li$^+$ by −32.9 kcal/mol. In the final dimer species (Figure 4b), the Li $^+$ cation is located on top of the cyclobutane ring, and the C$_{120}$ is negatively charged.

The inter-radical combination reaction of two C$_{60}^-$Li$^+$ radical ion pairs was also examined. Although ΔH_f^o(r) in the formation of C$_{120}^{2-}$(Li$^+$)$_2$ from two C$_{60}^-$Li$^+$ is calculated to be exothermic by 57.7 kcal/mol, that of the intermediate state (C$_{60}$—C$_{60}$)$^{2-}$-(Li$^+$)$_2$ having a single pivot bond is endothermic by 69.0 kcal/mol with respect to two C$_{60}^-$Li$^+$. Therefore, this process seems to be unlikely to occur in the initial stage of the electrochemical deposition of polymerized C$_{60}$. The initial stage of the polymerization of C$_{60}$ phase seems to be the process schematically

high-energy shift should be expected upon network formation,[22] a considerably low-energy shift was usually observed in pressure-induced polymers and especially in polymeric alkali fullerides. Only the photoinduced C$_{60}$ polymer is known to maintain a broad IR mode close to 1424 cm^{-1}.[20,21] We associate the observed spectral features with structural modification to C$_{60}$ structure.

As can be seen in the Raman spectrum shown in Figure 3, the baseline shift suggests the film was weakly photoemissive. The dominant features are two lines at 1459 and 1570 cm^{-1}. The former line is known to result from a downshift of the strong A$_g$ pentagonal pinch-mode line of molecular C$_{60}$ (1469 cm^{-1}) and has been established as both a qualitative and quantitative measure of the symmetry-reduced polymerized state.[20,21,23,24] In alkali metal doped polymer films, a frequency shift of −6 cm^{-1} per electron occurs due to the charge transfer as well. The higher frequency line at 1570 cm^{-1}, also visible as the second dominant line in Raman studies of photoinduced, plasma-induced, or pressure-induced C$_{60}$ polymers,[20,21,23,25] is a typical indication of the presence of a weakly conjugated C=C double bond.[25] The vibrational features in Figure 3 compare favorably with those of plasma-polymerized C$_{60}$,[25] providing strong evidence for the presence of a polymerized state of C$_{60}$.
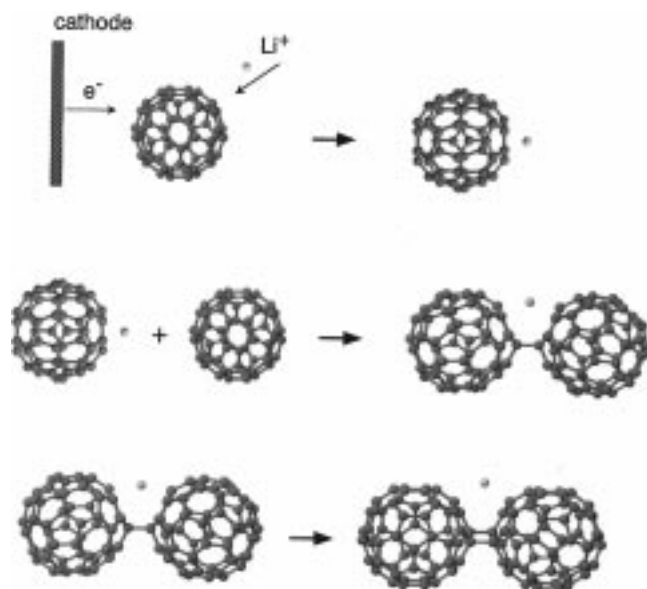
Figure 5. Possible initial formation process of and polymerization of $C_{60}Li$.

shown in Figure 5. Finally, the electrochemically prepared films must be a randomly polymerized phase brought about by the succeeding radical addition of the $C_{60}^-Li^+$ radical ion pair.

The calculations also suggest that small movement of Li^+ causes a significant change in the electronic structure of $C_{120}^-Li^+$ shown in Figure 4b, especially in peripheral carbon atoms of Li^+. The symmetric C−C stretching mode of the cross-linking should Raman-active, although this mode was not observed. This could be because of the Li^+ participate in the intermolecular cross-linking and/or limited number of the bonds as well.

4. Conclusions

An electrochemical synthetic route has been presented which led to the formation of a insoluble carbon thin film upon electroreduction of a solution of C_{60}. Spectroscopic evidence has been given that intact C_{60} cages in a partially charged, symmetry-reduced state as well as Li^+ cations are present in the film. It is concluded that the electroreduction process has led to the formation of a negatively charged polymerized phase of C_{60} intercalated by Li^+ counterions. Numerical investigation of a detailed mechanistic pathway to $C_{120}^-Li^+$ ion-pair dimers supported the thermodynamical feasibility of the reaction sequence. Due to asymmetric charge distribution in $C_{120}^-Li^+$, further radical addition to the dimer is favored, thus accounting for the growth of polymeric C_{60} phase.

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