

## Electrochemical Doping of Lithium Ions Into Pressure-Polymerized Fullerenes

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Several pressure-polymerized  $C_{60}$  phases were prepared by high pressure and high temperature treatments. The electrochemical intercalation experiments of lithium into the  $C_{60}$  polymers were performed. The cyclic voltammograms of the  $C_{60}$  polymers were also observed and compared with that of pristine  $C_{60}$  powder sample. In order to characterize the reduced  $C_{60}$  polymers, XRD and XPS measurements were carried out.

Key words:  $C_{60}$ , Fullerene polymer, Lithium, Cyclic voltammetry

### 1. INTRODUCTION

It is known that solid  $C_{60}$  (fcc- $C_{60}$ ) is transformed into polymerized phases by high pressure and high temperature treatment[1-4]. So far, at least three crystalline phases (rhombohedral, orthorhombic and tetragonal phases) and some amorphous phases of pressure-polymerized fullerene were synthesized[5,6]. For convenience, we use abbreviations such as *o*- $C_{60}$ , *rh*- $C_{60}$  and *a*- $C_{60}$  to express orthorhombic, rhombohedral and the amorphous  $C_{60}$  polymers.  $C_{60}$  molecules in *o*- $C_{60}$  and *rh*- $C_{60}$  are connected each other one- or two-dimensionally, respectively. *a*- $C_{60}$  polymers are synthesized under extreme conditions and cage structure of  $C_{60}$  molecule is considered to be collapsed. These polymerized fullerene are expected to produce new functional materials by intercalation technique[7,8]. However, as the  $C_{60}$  polymers are easily degraded into monomers at elevated temperatures[1,9], it is difficult to synthesize the intercalated  $C_{60}$  polymer by ordinary chemical methods.

$C_{60}$  molecule has triply-degenerate states both in lowest and second lowest unoccupied molecular orbitals (LUMO and LUMO+1). Because the orbital energy of LUMO is considerably low, it is rather easy to produce charge transfer complexes using alkali metals. In fact, it was reported that  $Li_{12}C_{60}$  can be produced by the electrochemical intercalation of

lithium ions into fcc- $C_{60}$ [10]. From the industrial point of view, fcc- $C_{60}$  has been expected as an anode material of lithium secondary battery, because the Li / C ratio of the fulleride was greater than that of the graphite intercalation compound  $LiC_6$ . However, there is a significant problem for practical application since fcc- $C_{60}$  is soluble in most liquid electrolytes. On the other hand, the solubility of the  $C_{60}$  polymers into liquid electrolytes are very low. Furthermore, the  $C_{60}$  polymers have large structural space for Li ions to be intercalated. Therefore, the  $C_{60}$  polymers could be an alternative candidate for the anode material. However, the electrochemical properties of the  $C_{60}$  polymers have not been well investigated. In this paper, We report on the results of the electrochemical experiments of the  $C_{60}$  polymers.

### 2. EXPERIMENTAL

An fcc- $C_{60}$  powder sample (Hoechst > 99.78 %) charged in a Pt capsule was compressed by using a multi-anvil high pressure apparatus up to 5 GPa and then heated at expected temperatures for 1 h. Subsequently, the sample was cooled down to room temperature, followed by the release of the pressure.

Electrochemical measurements of the  $C_{60}$  polymers were performed at room temperature in a three electrode cell. A Li (Aldrich 99.7%) wire and a Li disk were used as a reference electrode (RE) and a

counter electrode (CE), respectively. A mixture of the  $C_{60}$  polymer powder and polyvinylidene fluoride (PVDF: Kureha chem.) binder (9 : 1 volume ratio) cast on a Cu disk was used as a working electrode (WE). The electrolyte solution was 1M  $LiClO_4$  (Wako 98.0%) in an ethylene carbonate (EC) + diethyl carbonate (DEC) mixture (1 : 1 volume ratio) purchased from Mitsubishi Chem. (high purity Li battery grade). To avoid the dissolution of fcc- $C_{60}$  into the liquid electrolyte, we carried out the electrochemical experiment of fcc- $C_{60}$  with all solid state cell using polyethylene oxide (PEO Mw = 900000) purchased from Aldrich. The cell was constructed with a Li disk CE, the polymer electrolyte film prepared by the mixture of PEO and  $LiClO_4$  ( $P(EO)_{20}LiClO_4$ ), and a composite WE containing fcc- $C_{60}$  and electrolyte, cast from acetonitrile (Wako) suspension onto a stainless steel current collector. The solid state cell was operated at 80°C to maintain the electrolyte in the high ionic conductive phase. All the electrochemical experiments were performed in an argon dry box.

In order to characterize the reduced  $C_{60}$  polymers, XRD and XPS measurements were performed on a conventional powder diffractometer (Rigaku RINT-2200) and a SHIMAZU ESCA-750, respectively. For XRD measurements, the composite WE taken from the cell was dried in vacuum and then sealed with polyethylene bag under Ar atmosphere to avoid the exposure to air. Since the XPS spectrometer has an introduction chamber, the samples were able to be kept in Ar gas.

### 3. RESULTS AND DISCUSSIONS

Fig. 1 shows the observed cyclic voltammograms (CV) of  $rh-C_{60}$ . In the second and third cycle, only three reversible redox peaks having  $E_{1/2} = 170, 650, 1005$  mV which may be attributed to Li intercalation / de-intercalation were observed. On the other hand, some irreversible reduction currents are also seen in the first cycle. It is considered that the currents due to the reduction of impurities (e.g.  $H_2O$ ) and the formation of solid-electrolyte interphase (SEI) flow in the range of 2 – 1.5 V and at around 1 V, respectively.

The first discharge curve of  $rh-C_{60}$  is shown in Fig.2 with those of  $o-C_{60}$  and  $a-C_{60}$ . As shown in Fig. 2, Li can be doped into  $rh-C_{60}$  apparently up to the composition of  $Li_3C_{60}$ . However, if the first reduction of  $rh-C_{60}$  occurs at around 0.82 V (Fig. 1),  $x$  in  $Li_x(rh-C_{60})$  should be less than 3. The increase of Li content in the WE with increasing reduction time was confirmed by Li 1s XPS measurements (Fig. 3). Unfortunately, it is difficult to determine the composition of the doped  $rh-C_{60}$  by XPS measurement, because we used PVDF as a binder and could not

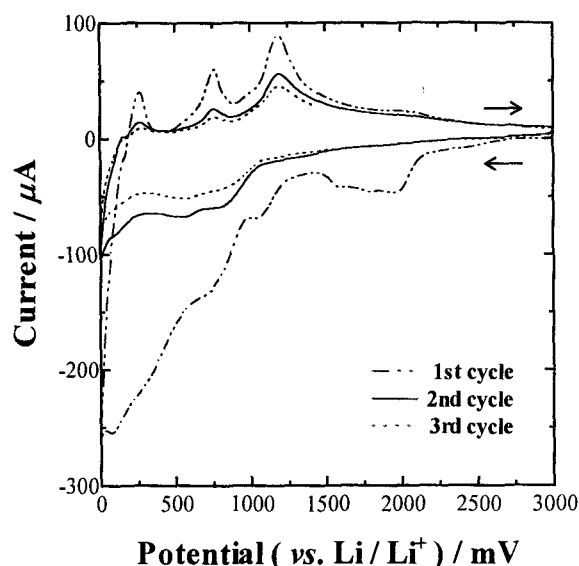


Fig. 1 The observed cyclic voltammograms of  $rh-C_{60}$  obtained at a potential scan rate  $v = 50 \mu V s^{-1}$ .

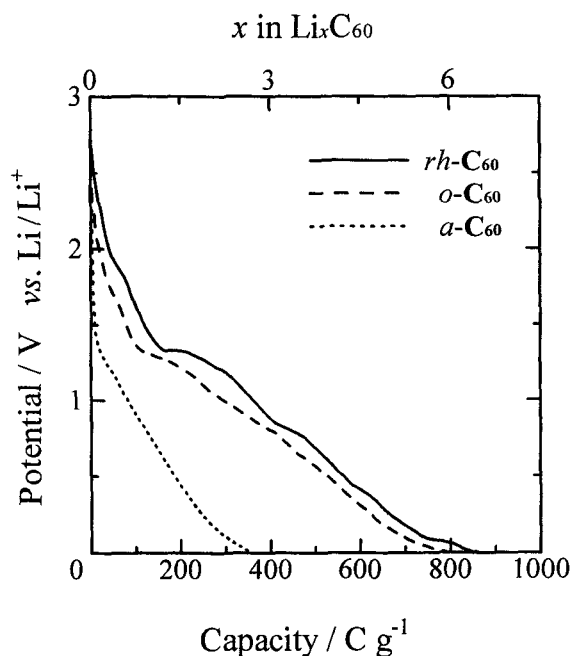


Fig. 2 Potential vs. charge for  $Li_xC_{60}/LiClO_4-EC+DEC/Li$  cell. The doping level  $x$  is also indicated at the top of axis of the plot.

obtain reliable Li / C values. No remarkable change in the XRD pattern of  $rh-C_{60}$  with Li doping was observed (Fig. 4). It was also found that the lattice parameters before and after the doping are almost the same. Núñez et al[2]. proposed the model structure of  $rh-C_{60}$  having  $R\bar{3}m$  space group. According to their model, the  $o$ -site and  $t$ -site correspond to 3b and 6c sites in Wyckoff notation, respectively. Although the  $z$  coordinate of 6c site is not determined uniquely, we

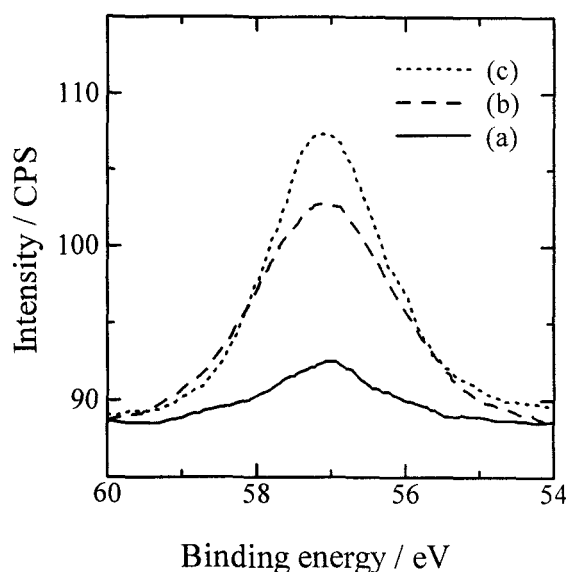


Fig. 3 The observed  $\text{Li } 1s$  XPS spectra of the reduced  $rh\text{-C}_{60}$ . Sample (a) is immersed in the electrolyte. Samples (b) and (c) are reduced up to their cell potential of 0.75 and 0 V, respectively.

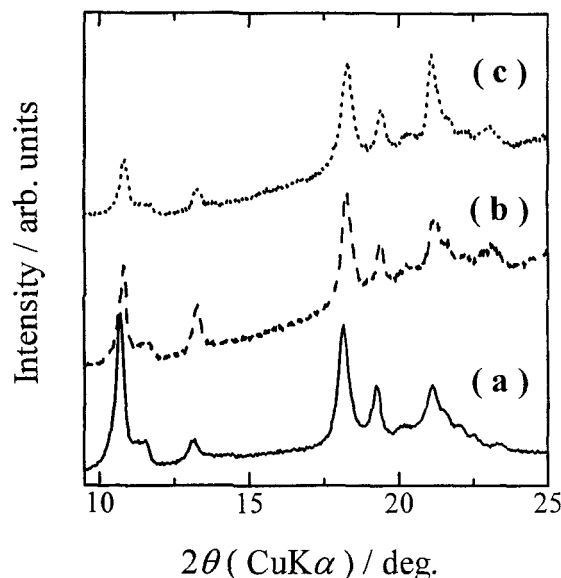


Fig. 4 The observed XRD patterns of the reduced  $rh\text{-C}_{60}$ . The notations are the same as in Fig. 3.

assume the  $t$ -site of  $z=0.215$  to keep equivalent distances from the carbon atoms of the nearest  $\text{C}_{60}$  clusters. Since the distance from the  $o$ -site and  $t$ -site of  $rh\text{-C}_{60}$  to the nearest carbon atom are calculated to be about 3.4 and 2.5 Å, respectively. These two sites have enough large void for Li ion to be intercalated. Fig. 5 shows the calculated XRD patterns of  $\text{Li}_x(rh\text{-C}_{60})$  assuming Li atoms in  $\text{Li}(rh\text{-C}_{60})$  and  $\text{Li}_3(rh\text{-C}_{60})$  occupy only  $o$ -site and both  $o$ -site and  $t$ -sites,

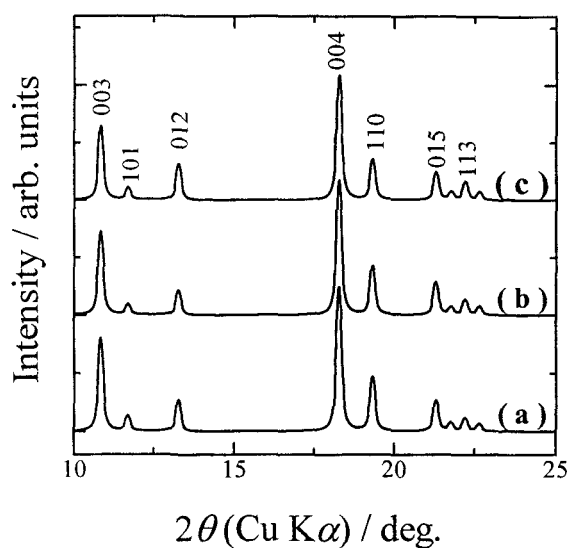


Fig. 5 The simulated XRD patterns of (a)  $rh\text{-C}_{60}$ , (b)  $\text{Li}(rh\text{-C}_{60})$  and (c)  $\text{Li}_3(rh\text{-C}_{60})$ .

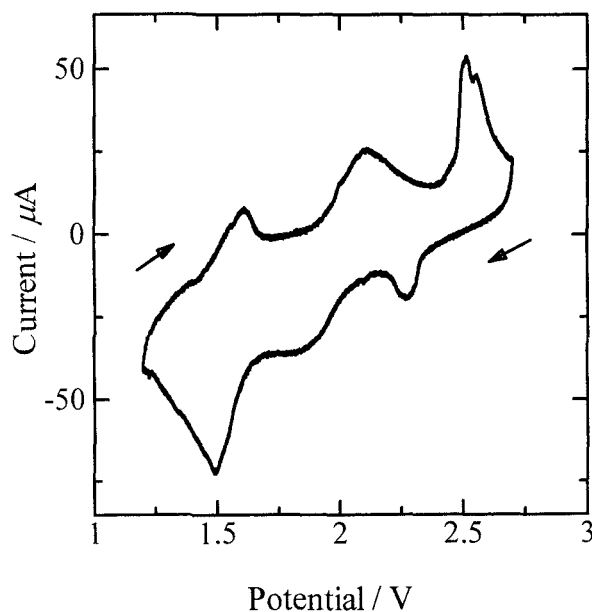


Fig. 6 Cyclic voltammogram of  $\text{fcc-C}_{60}$  obtained at scan rate  $\nu = 50 \mu\text{Vs}^{-1}$ .

respectively. There is only a little difference between the patterns in Fig. 5. Therefore, it would be difficult to confirm the existence of Li ions by XRD measurements.

In the case of  $\text{fcc-C}_{60}$ , Chabre et al[10], reported that it is possible to obtain  $\text{Li}_{12}\text{C}_{60}$  by electrochemical doping. The Li doping level of  $rh\text{-C}_{60}$  in the present study is much less than that of  $\text{fcc-C}_{60}$ . The CV diagram of  $\text{fcc-C}_{60}$  was observed so as to understand

the difference (Fig. 6). As shown in Fig. 6, the first reduction peak of fcc-C<sub>60</sub> is observed at around 2.3 V which is about 1.5 V higher than that of rh-C<sub>60</sub>. It is considered that the easier reduction of fcc-C<sub>60</sub> leads to the higher doping level. Assuming that the first reduction occurs by the electron transfer from an electrode to the bottom of the conduction band of fullerene and the difference between the overpotentials for rh-C<sub>60</sub> and fcc-C<sub>60</sub> reductions is negligible, the difference in the first reduction potentials of the two phases indicates that the bottom energy of the conduction band of fcc-C<sub>60</sub> is much lower than that of rh-C<sub>60</sub>. On the other hand, the theoretical calculation by using the local-density approximation (LDA)[7,11] shows that the band gap energy of rh-C<sub>60</sub> is 0.7 eV smaller than that of fcc-C<sub>60</sub> and that the total energies of these two phases are almost the same. It seems unreasonable to expect such a big difference between the bottom energies of the conduction bands of the two phases as mentioned above, although absolute band energy is not available by the LDA calculation. More precise experiments would be expected to discuss the electronic structures of the C<sub>60</sub> polymers.

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