Structural and electrochemical properties of fullerene C_{60} and fluorinated fullerenes treated at high pressure and high temperature

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Solid fullerene C_{60} consists of extremely hard pseudospherical molecules bound by weak van der Waals interaction. Owing to the weak intermolecular bonding and the molecular hardness, solid C_{60} had been expected to be solid lubricant which would be used under high pressure at high temperature where liquid lubricant can not be used. However, it been found difficult to use C_{60} as solid lubricant because solid C_{60} easily polymerizes under high pressure at high temperature [1, 2]; High pressure and high temperature treatment of solid C_{60} leads to various one- and two-dimensional polymers. Two-dimensional polymers (rhombohedral and tetragonal phases) have a layered structure like graphite. Therefore, they are expected to be used as electrode of lithium secondary battery. On the other hand, fluorinated fullerenes, bucky balls decorated with various numbers fluorine atoms, have also been expected to be used as new functionality materials including solid lubricant. In this work, we report on the structural and electrochemical properties of C_{60} and fluorinated fullerenes treated at high pressure and high temperature using in-situ X-ray measurements.

The lattice volume changes measured in-situ X-ray diffraction under high pressure in Figure 1 were fitted to the Birch-Murnaghan equation of state [3]. B_0 and B_0' of $C_{60}F_{36}$ and $C_{60}F_{48}$ were determined to be 15.2 GPa and 4.9, 4.8 GPa and 33.7, respectively. These values indicate that $C_{60}F_{36}$ and $C_{60}F_{48}$ are softer materials than C_{60} (B_0 = 15.6 GPa).

Figure 2 summarized structural stability of fullerene C_{60} and fluorinated fullerenes under high pressure and high temperature. The stable region of molecular fluorinated fullerenes is much larger than that of C_{60}, indicating that fluorinated fullerenes have much possibilities as solid lubricant.

Figure 3 shows cyclic voltammograms (CV) of two-dimensional rhombohedral polymers (*rh*-C_{60}) using 1M $LiClO_4$ / EC + DEC electrolyte [4]. In the second cycle, three reversible redox peaks having $E_{1/2}$ = 170, 650, 1005 mV attributable to Li intercalation / de-intercalation were observed. On the other hand, some irreversible reduction currents were also observed in the first cycle. They are attributed to the reduction of impurities (e.g. H_2O) and the formation of solid-electrolyte interphase (SEI) in the range of 2 – 1.5 V and at around 1 V, respectively.

Acknowledgement

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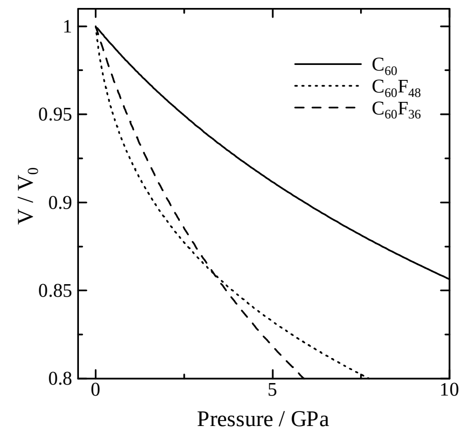

Fig. 1. Equation of state for C_{60}, $C_{60}F_{36}$ and $C_{60}F_{48}$ fitted to the Birch-Murnaghan equation of state.

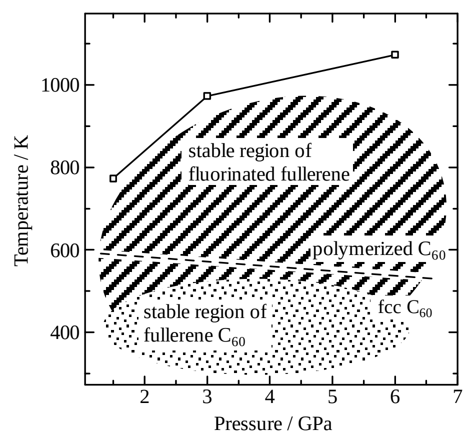

Fig. 2. Phase diagram of fluorinated fullerenes and fullerene C_{60}. Solid curve indicates amorphization temperature of fluorinated fullerenes as a function of pressure. Dashed line indicates the phase boundary between fcc-C_{60} and polymerized C_{60}.

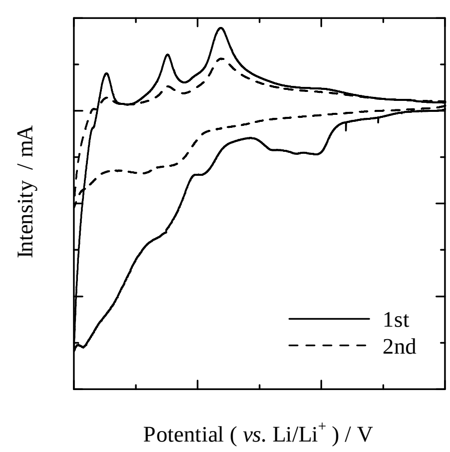

Fig. 3. Cyclic voltammograms of *rh*-C_{60} obtained at a potential scan rate v = 50 μVs^{-1}. The electrolyte used was 1M-$LiClO_4$ / EC + DEC.