

Fluorination of fullerenes C_{60} and C_{70} , the nature of C–F bond and electrochemical characteristics of $C_{60}F_x$ - and $C_{70}F_x$ -lithium cells

H. Touhara^a, F. Okino^a, S. Yajima^a, S. Suganuma^a, K. Seki^b, R. Mitsumoto^b and H. Fujimoto^c

^aDepartment of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan

^bDepartment of Chemistry, Faculty of Science, Nagoya University, Nagoya 464 Japan

^cResearch and Development Center, Osaka Gas Co., Ltd., Osaka 554, Japan

Fluorinated fullerene polycrystalline powders $C_{60}F_x$ and $C_{70}F_x$ ($20 < x < 49$) have been obtained by the direct fluorination or the fluorination in the presence of HF and/or AsF_5 , at 10 to 200°C. The value of x and the nature of C–F bonds, of which there are two kinds (semi-ionic and covalent), in $C_{60}F_x$ and $C_{70}F_x$ primarily depend on the fluorination temperatures and times.

The cyclic voltammogram of $Li/C_{60}F_{40}$ cell in $LiClO_4$ -propylene carbonate solution exhibits two irreversible reduction peaks at 3.25 and 2.80 V vs. Li reference at the scan rate of 1 mV/s. The former corresponds to the reduction of the semi-ionic C–F bonds, and the latter, the reduction of the covalent C–F bonds. The cell shows a remarkably high open circuit voltage of 3.99 V, which gives an extremely high theoretical energy density of 2890 Wh/kg-cathode. The cell stably discharges at 3.6 V under a load of 0.1 mA/cm² indicating a lower cathode overpotential.

1. INTRODUCTION

We have been making extensive studies on graphite intercalation compounds with fluorine and fluorides [1–2], and our studies based on graphite intercalation chemistry and fluorine chemistry have recently been extended to fluorine- and fluorides-fullerene systems [3].

An attractive feature of fullerenes is interactions of their π electron systems with F_2 , F_2/HF and penta- or hexafluorides with high electron affinity, that will give a very broad array of fluorides or charge transfer complexes of fullerenes. Stoichiometries, structures, properties and manifestation of functionality of resulting compounds are of great interest.

Recently, four experimental papers have described the fluorination of C_{60} or C_{70} [4].

In this study, we report the fluorination of C_{60} and C_{70} by elemental fluorine, F_2/HF and F_2/AsF_5 systems, stoichiometries, the nature of

C–F bond and electrochemical properties of $C_{60}F_x$ and $C_{70}F_x$.

2. EXPERIMENTAL

Fullerene polycrystalline powders (C_{60} and C_{70}) were reacted with 1 atm elemental fluorine at room temperature (RT)–200°C for 4 hours to 14 days or with 0.3–0.5 atm gaseous mixture of AsF_5/F_2 at RT for 10 days, in the nickel reaction tubes equipped with the stainless steel (SUS316) vacuum line. Fluorinations were also carried out in the Kel-F U-tubes in which fullerene powders were dispersed in liquid HF. Fluorine gas was admitted to flow in the tubes at 10°C for several hours and, reaction systems were allowed to stand for *ca.* 30 days.

The compositions of the samples were determined by XPS peak area ratio of C_{1s} , F_{1s} and As_{3d} or by chemical analysis on F

employing the oxygen flask combustion method with a fluoride ion electrode.

As fullerenes and fluorinated fullerenes have no electrical conductivities, the mixed electrodes were prepared as follows. Each sample was mixed with acetylene black as conductive additive and polyethylene powder as binder (2:1:1 in weight ratio), and the mixture was then pressed to form a pellet-electrode. The electrochemical properties have been investigated by the cyclic voltammetry and galvanostatic discharges of Li/C_{60} , $\text{Li}/\text{C}_{60}\text{F}_x$, $\text{Li}/\text{C}_{70}\text{F}_x$ cells in 1M LiClO_4 -propylene carbonate (PC) solution.

3. RESULTS AND DISCUSSION

3.1. Stoichiometry and the nature of C-F bond

The values x in C_{60}F_x and C_{70}F_x increase with increasing fluorination temperature and time. After extended fluorination times in the temperature range between RT and 200°C , C_{60} and C_{70} powders, respectively, yield C_{60}F_x ($20 < x < 47$) and C_{70}F_x ($32 < x < 49$). The values x of C_{70}F_x are always larger than those of C_{60}F_x at the same reaction temperature. With increasing temperature, the color varies from black through brown black to whitish yellow. The fluorinations in liquid HF at 10°C give whitish yellow $\text{C}_{60}\text{F}_{27}$ and $\text{C}_{70}\text{F}_{36}$. The interaction of C_{60} powders with AsF_5/F_2 gas mixture at RT gives lustrous blue compounds with nominal composition $\text{C}_{60}\text{AsF}_6$, indicating a kind of charge transfer complex. The color is exactly the same as that of the low stage graphite intercalation compounds of AsF_5 .

Fully fluorinated fullerenes $\text{C}_{60}\text{F}_{60}$ and $\text{C}_{70}\text{F}_{70}$, have not been obtainable yet by the routes so far employed.

The nature of C-F bonds in fluorinated fullerenes are of great interest. Here, we present in Figure 1 a representative C_{1s} XPS spectrum of C_{60}F_x ($20 < x$) obtained by the reaction of C_{60} with elemental fluorine. The peak **a** with the C_{1s} electron binding energy of 284.6 eV, which is almost the same as that of

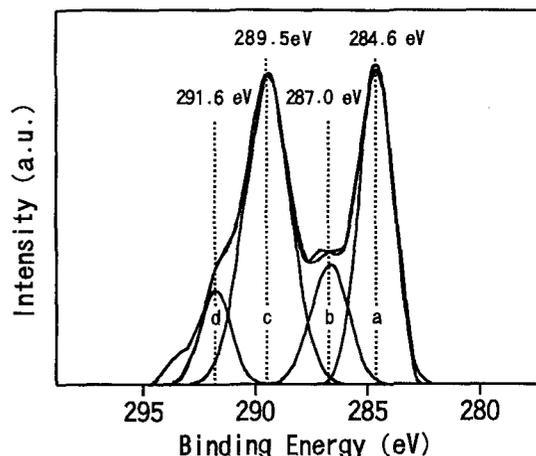


Figure 1. XPS spectra of $\text{C}_{60}\text{F}_{36}$ obtained by 24 h fluorination at 150°C

pristine C_{60} , is due to the carbon atoms with sp^2 -hybridization, without C-F bonds. The peak **c** is ascribed to sp^3 -hybridized carbon atoms with completely covalent C-F bonds which are fully characterized in the covalent compounds of graphite with fluorine, $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$ [1]. The C_{1s} electron binding energy of peak **b** lies between those of sp^3 - and sp^2 -hybridized carbon atoms. We have called them "carbon atoms with semi-ionic C-F bond" in low stage fluorine-graphite intercalation compounds C_xF ($x < 6$) [5]. The bond order in the semi-ionic bond is less than 1.0 and the bond length will be longer than that of typical covalent C-F bond. These features of the C_{1s} spectrum are common for C_{70}F_x . In addition to three peaks (**a**, **b**, **c**), the C_{60}F_x prepared by fluorinations at higher temperatures than *ca.* 100°C show the peak **d** with higher C_{1s} electron binding energy (*ca.* 292 eV) than that of the covalent C-F bond. This peak is assigned to $>\text{CF}_2$ carbon [1], suggesting some cleavages of the fullerene cage upon high temperature fluorinations.

In the case of $\text{C}_{60}\text{F}_{36}$ shown in Figure 1, the XPS spectrum indicates that the ratios of the carbon atoms with covalent and semi-ionic C-F bonds and without C-F bond are 2:1:2. Based on this result and on the assumed T_h

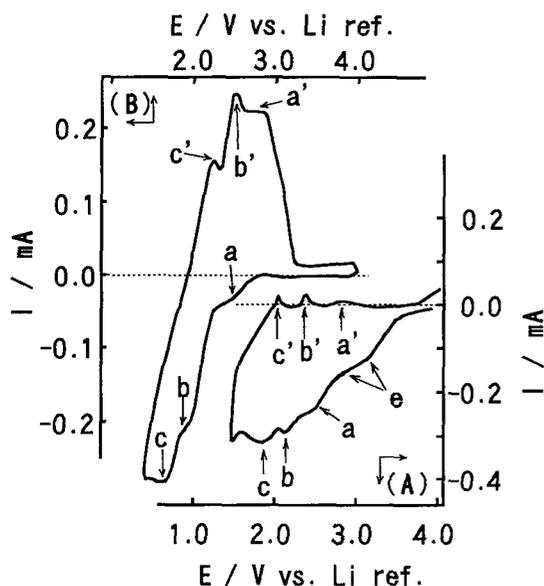


Figure 2. Cyclic voltammograms of (A) Li/C_{60} -powder; (B) $\text{Li}/\text{C}_{60}\text{F}_{40}$ -powder cells in 1M LiClO_4 -PC solution at 1 mV/s sweep rate. The working electrode area is 0.50 cm^2 .

symmetry of $\text{C}_{60}\text{F}_{36}$ with twelve isolated $\text{C}=\text{C}$ double bonds, one in each pentagon, $\text{C}_{60}\text{F}_{36}$ is composed of six islands with the composition of C_{14}F_6 (eight of the carbon atoms are each shared by another island, making the composition C_{10}F_6). The large steric repulsion between neighboring F atoms in the islands is responsible for the semi-ionic C-F bonds with the longer C-F bonds.

In contrast with the C_{1s} spectra, the F_{1s} spectra of C_{60}F_x and C_{70}F_x have symmetric shape and the F_{1s} electron binding energy of ca. 688 eV is close to that of C-F covalent bond. Further studies, *ab initio* molecular orbital calculations in particular, are necessary for a better understanding of the nature of C-F bond in C_{60}F_x and C_{70}F_x .

3.2. Electrochemical properties

Figure 2 shows cyclic voltammograms of Li/C_{60} (A) and $\text{Li}/\text{C}_{60}\text{F}_{40}$ (B) cells in 1M LiClO_4 -PC solution. In the voltammogram (A) for pure C_{60} , three reversible oxidation

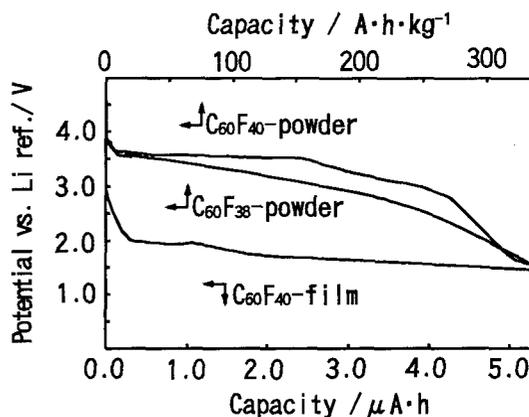


Figure 3. Discharge curves of $\text{Li}/\text{C}_{60}\text{F}_{40}$ -film, $\text{Li}/\text{C}_{60}\text{F}_{38}$ -powder and $\text{Li}/\text{C}_{60}\text{F}_{40}$ -powder cells in 1M LiClO_4 -PC solution under current densities of $10 \mu\text{A}/\text{cm}^2$, $500 \mu\text{A}/\text{cm}^2$ and $100 \mu\text{A}/\text{cm}^2$, respectively.

(**a'**:2.80, **b'**:2.37, **c'**:2.05 V)-reduction (**a**:2.50, **b**:2.15, **c**:1.85 V) peaks are observed in the sweep range of 1.0–4.0 V. The reduction peaks shift toward higher potentials by 0.2–0.3 V, indicating the changes in energy levels of HOMO and LUMO of C_{60} upon fluorination. In addition to three reversible peaks, $\text{C}_{60}\text{F}_{40}$ gives two irreversible reduction peaks (**e**:3.25, 2.80 V) which correspond to the reduction of the semi-ionic and covalent C-F bonds, respectively.

The discharge curves of $\text{Li}/\text{C}_{60}\text{F}_{40}$, $\text{C}_{60}\text{F}_{38}$ powders and $\text{C}_{60}\text{F}_{40}$ film in 1M LiClO_4 -PC are given in Figure 3. Among them $\text{C}_{60}\text{F}_{40}$ shows excellent discharge performances: a considerably high open circuit voltage (OCV) value 3.99 V and high discharge potential 3.6 V at a load of $100 \mu\text{A}/\text{cm}^2$, indicating the lower cathode overpotential. The problem, however, is the low cathode utilization of ca. 50 %. The $\text{Li}/\text{C}_{60}\text{F}_{60}$ cell with the OCV value of 3.99 V gives an extremely high theoretical energy density of 2890 Wh/kg-cathode, and the discharge performances of the $\text{Li}/\text{C}_{60}\text{F}_x$ cells could be improved by the optimum choice of solvent and electrolyte.

Acknowledgement

The authors wish to express their thanks to the Ministry of Education, Science and Culture of Japan for financial support by Grant-in-Aid for Carbon Clusters, Priority Area Research Program No. 05233215. One of the authors (FO) also thanks Research Foundation for Electrotechnology of Chubu for support.

REFERENCES

1. N. Watanabe, T. Nakajima and H. Touhara, *Studies in Inorganic Chemistry*, Vol. 8., Graphite Fluorides, Elsevier, Amsterdam, 1988.
2. H. Touhara, S. Suganuma, M. Ishihara and F. Okino, *New Functionality Materials: Design, Preparation and Control*, ed. by T. Tsuruta, M. Seno and M. Doyama, Elsevier, Amsterdam 1993 and references quoted therein.
3. F. Okino, H. Touhara, K. Seki, R. Mitumoto, K. Shigematsu and Y. Achiba, *Fullerene Science and Technology*, 1 (1993) in press.
4. A. A. Tuinman, P. Mukherjee, J. L. Adcock, R. L. Hettich and R. N. Compton, *J. Phys. Chem.*, 96 (1992) 7584 and references quoted therein.
5. H. Touhara, Y. Goto, N. Watanabe, K. Imaeda, T. Enoki, H. Inokuchi and Y. Mizutani, *Synthetic Metals*, 23 (1988) 461.