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Takashi Itoh [a], Ryo Yasuda [a], Takayuki Go [a], Shoji Nitta [a] & Shuichi Nonomura [b]

[a] Department of Electrical Engineering, Gifu University, 1-1 Yanaido, Gifu, 501-1193, Japan

[b] Environment and Renewable Energy Systems, Graduate School of Engineering, Gifu University, 1-1 Yanaido, Gifu, 501-1193, Japan

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# Intercalation of $O_2$ and its Effect on the Properties of $C_{60}$ and $C_{70}$ Solids

TAKASHI ITOH[a], RYO YASUDA[a], TAKAYUKI GO[a], SHOJI NITTA[a] and SHUICHI NONOMURA[b]

[a]*Department of Electrical Engineering, Gifu University, 1–1 Yanaido, Gifu 501–1193, Japan and* [b]*Environment and Renewable Energy Systems, Graduate School of Engineering, Gifu University, 1–1 Yanaido, Gifu 501–1193, Japan*

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The intercalation of $O_2$ in $C_{60}$ and $C_{70}$ solids have been studied. In both gas effusion spectra of $C_{60}$ and $C_{70}$ powder exposed to $O_2$ at room temperature, two evolution peaks of $O_2$ are found near 80 and 150°C. In both $C_{60}$ and $C_{70}$ powder, the peak near 80°C does not depend on a heating ratio and the peak near 150°C shifts to higher temperature with the heating ratio. The activation energy on diffusion of $O_2$ in $C_{60}$ and $C_{70}$ solids are ~0.27eV and ~0.46eV, respectively. The number of $O_2$ intercalated in $C_{70}$ powder is larger than that in $C_{60}$ powder. Electron spin density of 02-intercalated $C_{60}$ film is larger than that of $C_{70}$ film. The effect on the properties of $C_{60}$ and $C_{70}$ solids by the intercalation of $O_2$ are discussed.

*Keywords:* $C_{60}$ and $C_{70}$ solids; intercalation of 02; electron spin resonance; gas effusion spectroscopy; electrical conductivity

## INTRODUCTION

It is well known that $O_2$ are intercalated into $C_{60}$ solids in air and the properties, such as electrical conductivity, of $C_{60}$ solids vary by the intercalation of $O_2$ [1-3]. The properties of $C_{70}$ solids are also affected by the

intercalation of $O_2$. The intercalation of $O_2$ in $C_{60}$ and $C_{70}$ solids would be different, because of the difference in the molecular shape. Therefore it is important to understand the intercalation of $O_2$ into $C_{60}$ and $C_{70}$ solids in order to apply to electronic devices for $C_{60}$ and $C_{70}$ solids and to understand the intercalation of other materials such as an alkali metal. In this report, the intercalation of $O_2$ and its effect on the properties of $C_{60}$ and $C_{70}$ solids have been studied using gas effusion spectroscopy, electron spin resonance and electrical conductivity. The intercalation of $O_2$ and its effect on the properties of $C_{60}$ and $C_{70}$ solids are discussed.

## EXPERIMENTS

$C_{60}$ and $C_{70}$ powder (Term Co.) were used in gas effusion spectroscopy and as a source material on preparation of $C_{60}$ and $C_{70}$ films. The nominal purity of $C_{60}$ and $C_{70}$ powder were 99.98 and 99%, respectively. $C_{60}$ and $C_{70}$ films were prepared by a vacuum evaporation method in the vacuum of ~$2.0\times 10^{-5}$ Torr. The $C_{60}$ and $C_{70}$ source powder was sublimated at 400~450 and 450~500°C onto sapphire substrates, respectively. The substrate temperature was 250°C.

Gas effusion spectra were measured as described elsewhere [4, 5]. $C_{60}$ and $C_{70}$ powder were exposed to $O_2$ of 1.0 atm. at room temperature to intercalate $O_2$ after annealing at ~350 and ~400°C in vacuum of ~$10^{-5}$ Torr for 8 hours, respectively. The purity of $O_2$ was 99.99%.

Electron spin densities of $C_{60}$ and $C_{70}$ films were obtained by electron spin resonance (ESR). The thickness of $C_{60}$ and $C_{70}$ films were ~2.2 and ~4.1μm, respectively The electrical dark conductivity was measured in a vacuum of about $3\times 10^{-4}$ Torr. In this work, Au were evaporated as gap

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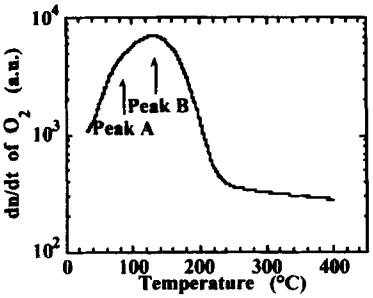


FIGURE 1 Gas effusion spectrum of $O_2$ for $C_{70}$ powder exposed to $O_2$ at room temperature for 48 hours.

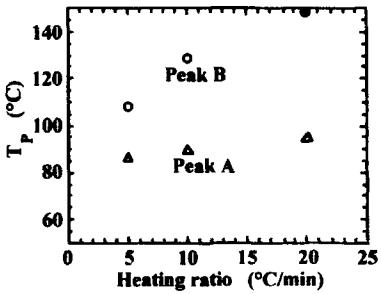


FIGURE 2 Dependence of peak temperature $T_P$ on heating ratio.

electrode with a gap of 60μm. The thickness of $C_{60}$ and $C_{70}$ films were ~2.5 and ~1.6μm, respectively. In both measurements, $C_{60}$ and $C_{70}$ films were exposed to $O_2$ of 1.0 atm. at room temperature after annealing at 200 and 300°C in vacuum of ~$10^{-5}$Torr for 8 hours, respectively.

## RESULTS AND DISCUSSION

Figure 1 shows a gas effusion spectrum of $O_2$ for $C_{70}$ powder exposed to $O_2$ for 48 hours. The heating ratio is 10 °C/min. In this spectrum, two evolution peaks of $O_2$ are found near 80 (peak A) and 150 °C (peak B). In that for $C_{60}$ powder exposed to $O_2$ at room temperature, two evolution peaks are also found near 80 and 150°C [4]. It is found that the evolution and absorption of $O_2$ in $C_{70}$ solids are reversible phenomena from the cyclic experiments. Figure 2 shows the dependence of the temperature $T_p$ of peaks A and B in fig.1 on heating ratio. The temperature of peak A is not almost dependent on heating ratio. The peak B shifts to higher temperature with the heating ratio. This result indicates that the evolution of $O_2$ for peak B would be controlled

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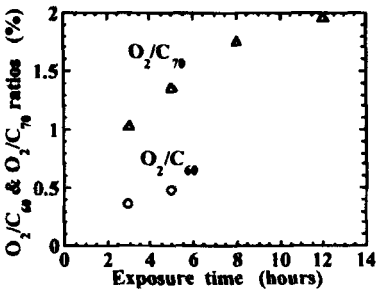


FIGURE 3 Dependence of $O_2/C_{70}$ and $O_2/C_{60}$ ratios in $C_{60}$ and $C_{70}$ powder on the exposure time to $O_2$.

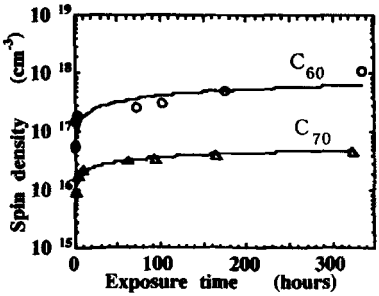


FIGURE 4 Dependence of electron spin density of $C_{60}$ and $C_{70}$ films on exposure time to $O_2$.

by a diffusion mechanism. Using this result, the activation energy on diffusion of $O_2$ in $C_{70}$ solid is determined as described in the previous report [4]. The activation energy on diffusion of $O_2$ in $C_{70}$ solid is ~0.46eV. The activation energy on diffusion of $O_2$ in $C_{60}$ solid is ~0.27eV [4]. Therefore $O_2$ is intercalated and evolved more easily in $C_{60}$ solids than $C_{70}$ solids. From gas effusion spectra, the oxygen-to-fullerene ratios, $O_2/C_{60}$ and $O_2/C_{70}$, are obtained using the method described in the previous report [4]. Figure 3 shows the dependence of $O_2/C_{60}$ and $O_2/C_{70}$ ratios in the samples on the exposure time to $O_2$ at room temperature. In this figure, both $O_2/C_{60}$ and $O_2/C_{70}$ ratios increase with exposure time to $O_2$. The number of $O_2$ intercalated in $C_{70}$ powder is larger than that in $C_{60}$ powder. This result could be explained as follows. In face-centered cubic (fcc) structure, there are one octahedral site (O site) per one fullerene molecule. In hexagonal closed packed (hcp) structure, there are two O sites per one fullerene molecule. The structure of used $C_{70}$ powder is mixture of fcc and hcp structures. The structure of $C_{60}$ solid is fcc. From previous result [4], $O_2$ is intercalated into O sites in $C_{60}$ solids at room temperature. Therefore $C_{70}$ powder has more intercalation sites and grain

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boundaries than $C_{60}$ powder at room temperature.

Figure 4 shows the dependence of the electron spin density of $C_{60}$ and $C_{70}$ films on the exposure time to $O_2$ at room temperature. In this figure, both electron spin densities of $C_{60}$ and $C_{70}$ films increase with the exposure time to $O_2$. The electron spin density of $O_2$-intercalated $C_{60}$ film is larger than that of $O_2$-intercalated $C_{70}$ film. From figs. 3 and 4, the intercalated $O_2$ would affect the properties of $C_{60}$ solids more than that of $C_{70}$ solids. These results could be explained as follows. The electron affinity of $C_{60}$ and $C_{70}$ solids are ~2.65 and ~2.72eV, respectively [5]. $O_2$ accepts electron from $C_{60}$ solids more easily than from $C_{70}$ solids. If the increase of the electron spin density by the intercalation is caused by the electron acceptance of $O_2$ from fullerene, the intercalated $O_2$ would affect the properties of $C_{60}$ solids than that of $C_{70}$ solids.

Figure 5 shows the dependence of the electrical conductivity of $C_{60}$ and $C_{70}$ films on the exposure time to $O_2$ at room temperature. The electrical conductivities of both $C_{60}$ and $C_{70}$ films decrease with the exposure time to $O_2$. This result on the $C_{70}$ film agrees with previously published data [6]. The decrease curve of the conductivity of the $C_{70}$ film is different from that of the

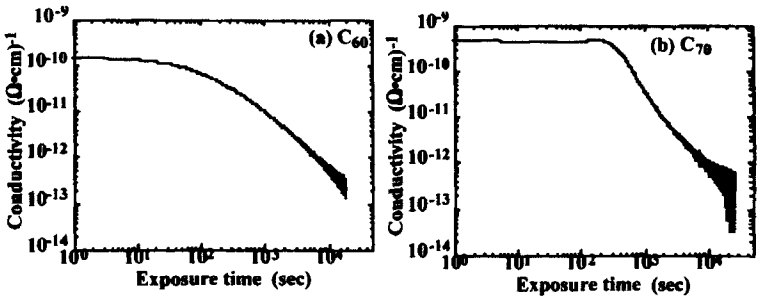


FIGURE 5 Dependence of electrical conductivity of (a) $C_{60}$ and (b) $C_{70}$ films on exposure time to $O_2$.

$C_{60}$ film. This result suggests that the intercalation mechanism of $O_2$ into $C_{70}$ solids would be different from that into $C_{60}$ solids. This difference could be caused by the difference in the molecular rotation and the crystalline structure.

## SUMMARY

The activation energies on diffusion of $O_2$ in $C_{60}$ and $C_{70}$ solids are ~0.27 and ~0.46eV, respectively. This result indicates that $O_2$ are intercalated and evolved more easily in $C_{60}$ solids than $C_{70}$ solids. The number of $O_2$ intercalated in $C_{60}$ and $C_{70}$ powder increases with the exposure time to $O_2$. The number of $O_2$ intercalated in $C_{70}$ powder is larger than that in $C_{60}$ powder. Electron spin densities of $C_{60}$ and $C_{70}$ films increase with the exposure time to $O_2$. Electron spin density of $O_2$-intercalated $C_{60}$ film is larger than that of $O_2$-intercalated $C_{70}$ film. Therefore the intercalated $O_2$ would affect the properties of $C_{60}$ solids more than that of $C_{70}$ solids.

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