

## Redox Behavior and Electron Affinity of Poly-epoxidated Fullerenes

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In the field of fullerene chemistry, electrochemistry of mono-epoxidated fullerene (**1**, in Fig. 1) has been paid much attention owing to its unique electronic properties. Therefore, various attempts were made for applications, e.g. photoelectronic devices using its high electron affinity.<sup>1</sup> However, electrochemistry of poly-epoxidated fullerenes ( $C_{60}O_n$ ) has never been studied so far because of the difficulty of additional position control and isolation. Recently, we have achieved the isolation of the several isomers of  $C_{60}O_n$  by means of HPLC using two different columns.<sup>2</sup> In this study, we carry out electrochemical analyses of regioselective  $C_{60}O_n$  which were isolated in our laboratory (Fig. 1) in order to reveal a mechanism of redox process of  $C_{60}O_n$  and a correlation between the electron affinity and the chemical structures of  $C_{60}O_n$ .

Electrochemical behavior of  $C_{60}O_n$  was observed by cyclic voltammetry with single and multi scanning and differential pulse voltammetry in an *o*-dichlorobenzene (DCB) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAF). All measurements were performed at 25 °C under a nitrogen atmosphere. A grassy carbon electrode (1.0 mm diameter) was used as the working electrode and a platinum wire was used as the counter electrode. The reference electrode was an Ag / 0.01 M  $AgNO_3$  electrode filled with 0.1 M tetrabutyl ammonium perchlorate in an acetonitrile solution.

Figure 2 shows the cyclic voltammogram of 1.0 mM compound **2a** in a DCB solution containing 0.1 M TBAF. The complicated redox wave due to side reactions of **2a** radical anion was observed. These side reactions were supported by the multicyclic voltammograms. Furthermore, in other  $C_{60}O_n$ , similar redox waves were observed. Such behavior of radical anion of  $C_{60}O_n$  is discussed on the basis of electrochemical study of **1** which causes electrochemical decomposition to  $C_{60}$  and electropolymerization.<sup>3</sup>

Figure 3 shows the half-wave potentials ( $E_{1/2}$ ) for the first reduction of  $C_{60}O_n$  determined by the differential pulse voltammetry versus LUMO energy levels of  $C_{60}O_n$  evaluated by the PM3 semiempirical molecular orbital calculation. The values of  $E_{1/2}$  increase with the decrease of LUMO energy levels since low LUMO energy suggests high electron affinity.<sup>4</sup> Furthermore,  $C_{60}O_n$  having the epoxy groups in large numbers or at neighbor position give noble reduction potentials (higher electron affinity). These correlations may be affected by the electron withdrawing effect by oxygen atom of epoxy group,<sup>4</sup> dipole moment, and strain energy arising from the fullerene structure.

### References

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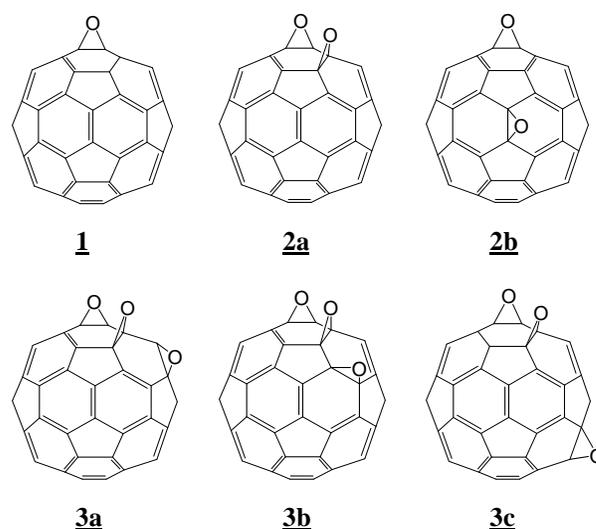


Fig. 1. Chemical structures of mono-epoxidated fullerene (**1**) and poly-epoxidated fullerenes (**2a-3c**).

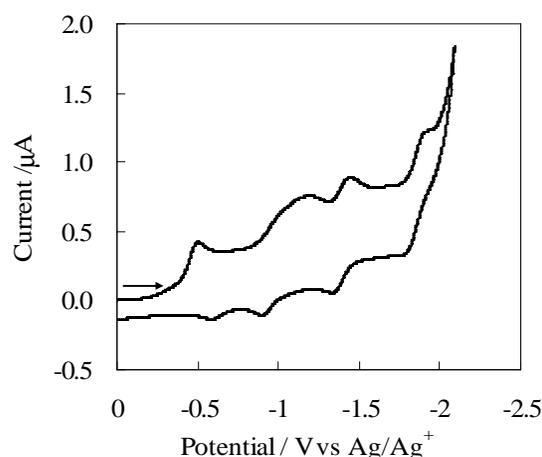


Fig. 2 Cyclic voltammogram of 1.0 mM compound **2a** in a DCB solution containing 0.1 M TBAF. Scan rate: 20  $mV s^{-1}$ .

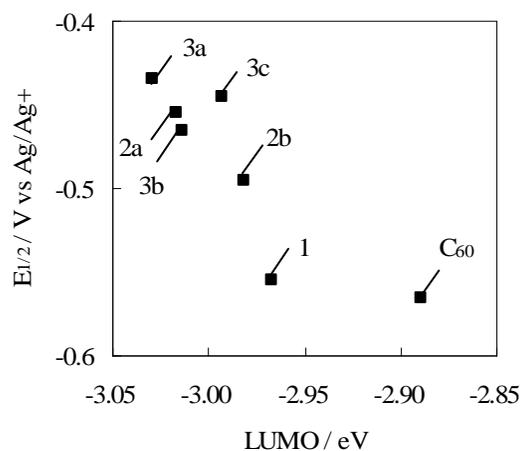


Fig. 3  $E_{1/2}$  for the first reduction of  $C_{60}O_n$  vs LUMO energy levels of  $C_{60}O_n$ .