Pergamon

Tetrahedron, Vol. 52, No. 14, pp. 4973-4982, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00105-6

Electrochemical Properties of Fullerenolanthanides

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Abstract: The cyclic voltammogram (CV) of $Y@C_{82}$ shows one reversible oxidation and four reversible reductions in 1,2-dichlorobenzene. The first redox potentials of $Y@C_{82}$ are anodically shifted by 30 and 50 mV, respectively, relative to those of $La@C_{82}$. As observed for $La@C_{82}$ and $Y@C_{82}$, the first redox processes of $Ce@C_{82}$ and $Gd@C_{82}$ are reversible by CV, and their potentials are also very close to those of $La@C_{82}$ and $Y@C_{82}$. It was found that the ionic radii of Ln^{3+} show good linear relationships with the first redox potentials of $La@C_{82}$, $Ce@C_{82}$, $Gd@C_{82}$, and $Y@C_{82}$. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Smalley and collaborators showed in 1991 that lanthanide-containing fullerenes (fullerenolanthanides) can be produced by laser vaporization of graphite and lanthanum oxide and extracted by toluene.[1,2] The following year, Johnson et al. found that $La@C_{82}$ is a radical species which exhibits eight EPR lines.[3] They suggested that the formal oxidation state of lanthanum is 3+ because of the small hyperfine constant. Later, more careful extraction under anaerobic conditions gave five different octet species; among them, two $La@C_{82}$ isomers are relatively stable molecules.[4-6] However, low yields, air-sensitivity, and difficulty of purification have prevented researchers from exploring the chemistry of these attractive molecules. Physical measurements, such as EPR,[3-9] mass spectrometry,[10-13] extended X-ray absorption fine structure (EXAFS),[14,15] and X-ray photoelectron spectroscopy (XPS),[7] were done with the extracts containing the mixture of fullerenolanthanides and empty fullerenes. Recently, Kikuchi et al.

succeeded in purifying La@C_{82} (major isomer with a hyperfine constant, 1.16 G) and an EPR-silent La_2@C_{80} in pure forms.[16,17] Independently, Yamamoto et al. obtained two La@C_{82} isomers (major and minor isomers with hyperfine constants, 1.16 and 0.84 G, respectively) and characterized them.[18,19] It was concluded that La@C_{82} is a semiconductor in the solid state by ultraviolet photoelectron spectroscopy (UPS) and XPS.[20,21] Although the structures of the fullerenolanthanides have not been determined, some theorists proposed that the lanthanide atom is not located in the center of the cage but is strongly coordinated by carbon atoms inside the cage (Figure 1).[22-24] To get further information of the electronic structures of the fullerenolanthanides, we performed electrochemical measurements and describe here unusual redox properties of the major isomers of La@C_{82}, Y@C_{82}, Ce@C_{82}, and Gd@C_{82} which significantly differ from those of empty fullerenes.[25,26]

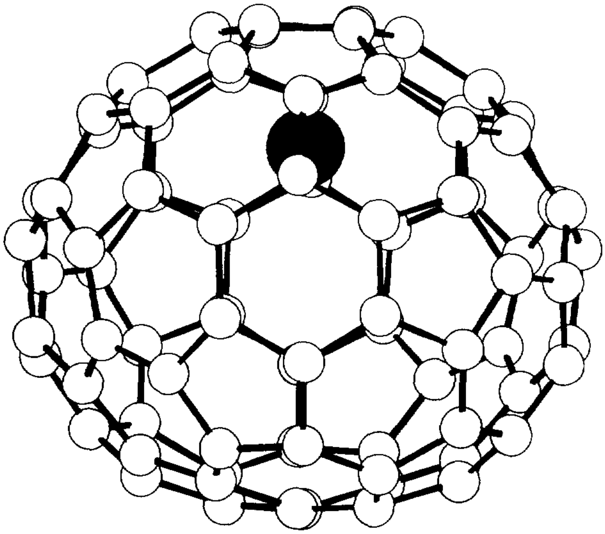

Figure 1. The C_2-structure of La@C_{82} obtained by ab initio calculations.

RESULTS AND DISCUSSION

Electrochemistry of La@C_{82}

Cyclic (CV) and differential pulse voltammograms (DPV) were recorded on a BAS-100B/W with a three-electrode configuration. We used 1,2-dichlorobenzene throughout the measurements because the solubility of the fullerenolanthanides is relatively high in this solvent. We first looked at the oxidation because we expected the series of three sequential one-electron steps due to C_{82}^{3-}. The scan started at the rest potential (-0.20 V vs ferrocene/ferrocenium couple) toward the positive potential. Two oxidation peaks at +0.05 and +1.07 V were observed by DPV, and the latter was irreversible by CV (Figures 2a and 3a and Table 1). Even faster scan rates up to 1000 mV/s did not improve the irreversibility of the second oxidation. The first reversible oxidation potential (+0.07 V) is slightly more positive than that of ferrocene, indicating that La@C_{82} is a good electron donor. The reduction of La@C_{82} was then examined. Surprisingly, it showed five reversible waves by CV, even though the formal charge of the C_{82} cage is already 3-. In addition, La@C_{82} is a stronger electron acceptor than empty fullerenes such as C_{60}, C_{70},[27-29] C_{76},[30] C_{82}, and C_{86} (Table 1).

Table 1. Redox Potentials of Fullerenolanthanides[a]

compd	${}^{ox}E2$	${}^{ox}E1$	${}^{red}E1$	${}^{red}E2$	${}^{red}E3$	${}^{red}E4$	${}^{red}E5$	${}^{red}E6$
La@C_{82}	+1.07[b,c]	+0.07	-0.42	-1.37	-1.53	-2.26	-2.46[c]	
Ce@C_{82}	+1.08[b,c]	+0.08	-0.41	-1.41	-1.53	-1.79	-2.25	-2.50[c]
Gd@C_{82}	+1.08[b,c]	+0.09	-0.39	-1.38[d]		-2.22[b,c,d]		
Y@C_{82}	+1.07[b,c]	+0.10	-0.37	-1.34[d]		-2.22	-2.47[c]	
C_{60}		+1.21[b,c]	-1.12	-1.50	-1.95	-2.41[c]		
C_{70}		+1.19	-1.09	-1.48	-1.87	-2.30		
C_{76}		+0.81	-0.94	-1.26	-1.72	-2.13		
C_{82}[e]		+0.72	-0.69	-1.04	-1.58	-1.94		
C_{86}[e]		+0.73	-0.58	-0.85	-1.60	-1.96		

[a] Half-cell potentials unless otherwise stated. Values are in volts relative to ferrocene/ferrocenium couple. Conditions: 0.1 M (n-Bu)$_4$NPF$_6$ in 1,2-dichlorobenzene; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M AgNO$_3$ and 0.1 M (n-Bu)$_4$NClO$_4$ in CH$_3$CN. CV: scan rate, 20 mV/s. [b] Irreversible. [c] Values were obtained by DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s. [d] Two-electron process. [e] The potentials are for the major isomer.

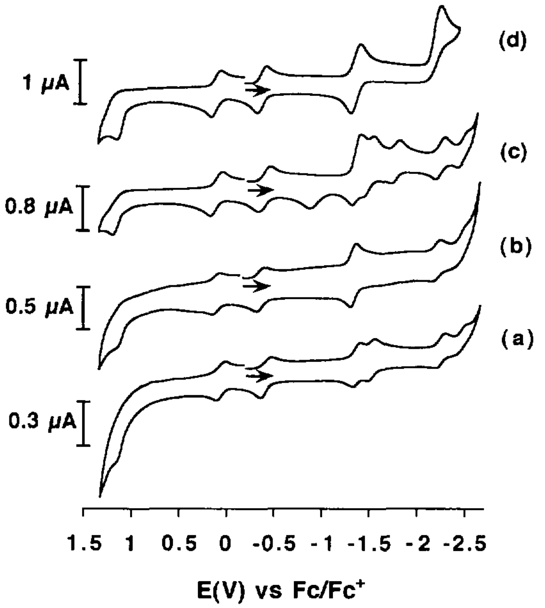

Figure 2. Cyclic voltammograms of (a) La@C_{82}, (b) Y@C_{82}, (c) Ce@C_{82}, and (d) Gd@C_{82} at 20 mV/s in 1,2-dichlorobenzene containing 0.1 M (*n*-Bu)$_4$NPF$_6$.

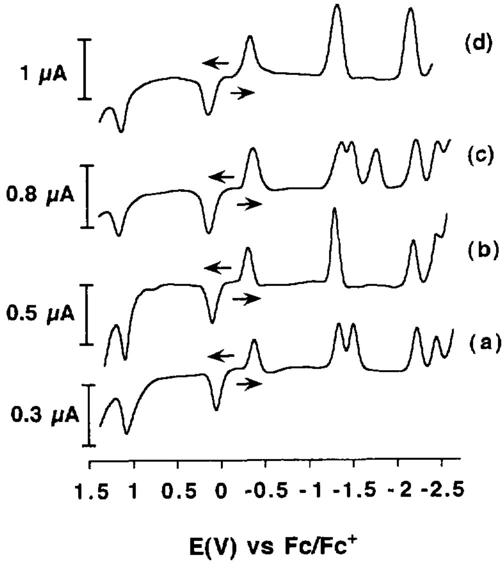

Figure 3. Differential pulse voltammograms of (a) La@C_{82}, (b) Y@C_{82}, (c) Ce@C_{82}, and (d) Gd@C_{82} in 1,2-dichlorobenzene containing 0.1 M (*n*-Bu)$_4$NPF$_6$.

Figure 4 shows a schematic MO diagram for La@C_{82}.[23,24] Assuming that all reversible redox processes observed involve a single electron, we may explain the results above by the following: (1) The removal of the radical electron corresponds to the first oxidation process. The resulting La@C_{82}^{+} should have no unpaired electrons. (2) The first reduction is relatively easy because an electron goes to the HOMO to give the closed-shell species La@C_{82}^{-}. (3) The low-lying HOMO-1 could be responsible for the irreversible formation of La@C_{82}^{2+} in our experiment. (4) The ab initio calculations on La@C_{82} show that the LUMO and LUMO+1 derive from the C_{82} MOs, not from 5d and 6s AOs of the lanthanum metal.[23,24] Therefore, we suggest that electrons at least up to the 5- state go to the C_{82} cage, not to the metal.

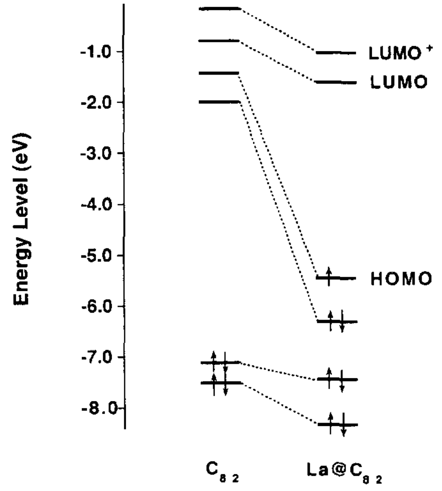

Figure 4. Schematic MO diagram for La@C_{82}.

Electrochemistry of Y@C_{82}

As seen in Figure 2b, one reversible oxidation and four reversible reductions were observed for Y@C_{82} by CV. The second oxidation remained irreversible at faster scan rates up to 1000 mV/s. By DPV (Figure 3b), the peak current intensity of the second reduction is twice that of each of the other redox peaks; the shape of the current voltage curve suggests a simultaneous two-electron transfer, not an overlap of two one-electron transfers.

In comparison with the electrochemistry of La@C_{82}, we would like to point out the following: Each of the metallofullerenes has a remarkably small potential difference between the first oxidation and the first reduction (Y@C_{82}, 0.47; La@C_{82}, 0.49 V). This may suggest that the HOMO of Y@C_{82}, originally the LUMO+ of the C_{82}, is singly occupied (i.e., SOMO) as proposed for La@C_{82} (Figure 4). Therefore, the oxidation state of the yttrium is close to that of the lanthanum, likely 3+.[31] The first oxidation and reduction potentials of Y@C_{82} are anodically shifted by 30 and 50 mV, respectively, relative to those of

$La@C_{82}$ (Table 1). These relatively small shifts are in agreement with the ab initio calculations which predict that the ionization potential and the electron affinity of $Y@C_{82}$ (6.22 and 3.20 eV, respectively) are almost the same as those of $La@C_{82}$ (6.19 and 3.22 eV, respectively).[31]

Electrochemistry of $Ce@C_{82}$ and $Gd@C_{82}$

As observed for $La@C_{82}$ and $Y@C_{82}$, the first redox processes of $Ce@C_{82}$ and $Gd@C_{82}$ are reversible, and their potentials are very close to those of $La@C_{82}$ and $Y@C_{82}$ (Table 1 and Figures 2 and 3). The second and third reductions of $Gd@C_{82}$ (-1.38 and -2.22 V) are two-electron processes, but the latter is irreversible. On the other hand, the second and third reductions of $Ce@C_{82}$ (-1.41 and -1.53 V) are irreversible even when the lowest potential of the scan is -1.6 V. Interestingly, after one reversible and two irreversible reductions, three other reversible reductions (-1.79, -2.25, and -2.50 V) were observed for $Ce@C_{82}$. Unlike $La@C_{82}$, $Y@C_{82}$, and $Gd@C_{82}$, the oxidation states of $Ce@C_{82}$ change from 2+ to 6-, not 5-, under the same conditions.

Relationship between the redox properties and the structures

The visible-near-IR absorption spectra of $Y@C_{82}$, $La@C_{82}$, $Ce@C_{82}$, and $Gd@C_{82}$ are very similar to each other and display characteristic near-IR bands due to their open-shell electronic structures (Figure 5). The two near-IR peaks are slightly shifted: $Y@C_{82}$, 990 and 1405; $La@C_{82}$, 1000 and 1420; $Ce@C_{82}$, 1015 and 1425; and $Gd@C_{82}$, 970 and 1400 nm. The similarities in the electronic spectra may indicate that they all have the same cage structures.

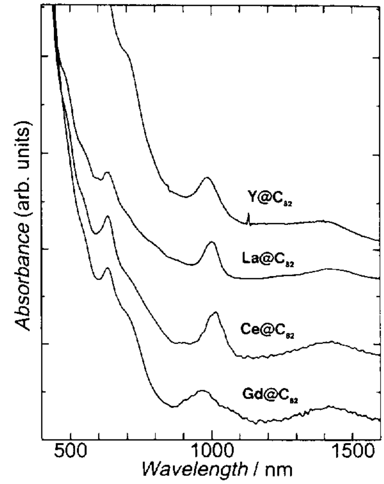

Figure 5. Comparative visible-near-IR absorption spectra of $Y@C_{82}$, $La@C_{82}$, $Ce@C_{82}$, and $Gd@C_{82}$ in toluene.

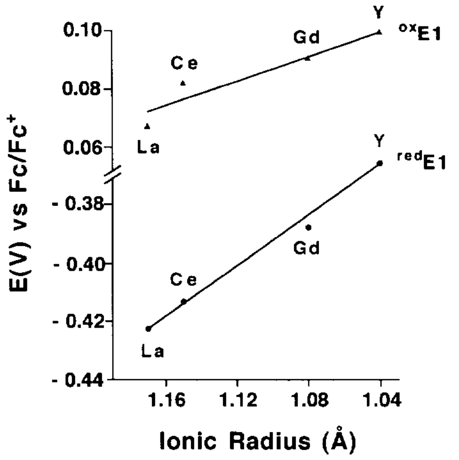

Figure 6. Plots of the first oxidation (above) and reduction potentials (below) of La@C_{82}, Y@C_{82}, Ce@C_{82}, and Gd@C_{82} vs the ionic radii of Ln^{3+}.

We plotted the first redox potentials of La@C_{82}, Y@C_{82}, Ce@C_{82}, and Gd@C_{82} vs the ionization potentials of the lanthanides,[32] the ionic radii of Ln^{3+} (six coordinate),[33] and the ionization potentials and electron affinities of the Ln@C_{82}s obtained by ab initio calculations.[31] It was found that the ionic radii of Ln^{3+} show good linear relationships with the first redox potentials (Figure 6). Assuming that (1) all four Ln@C_{82}s have the same cage structures, (2) the oxidation states of the metals are 3+, and (3) the metal-cage distances decrease in the order La > Ce > Gd > Y, one may explain these linear correlations as follows (Figure 7): The first oxidation and reduction processes take place on the SOMO whose electron density is higher on the cage close to the Ln^{3+}.[22-24] When the metal-carbon distance becomes shorter, the electrons on the SOMO are bound to the cage more strongly because of the electrostatic interaction between the electrons and the metal. This probably makes Y@C_{82} the poorest electron donor but the strongest electron acceptor among the four Ln@C_{82}s.

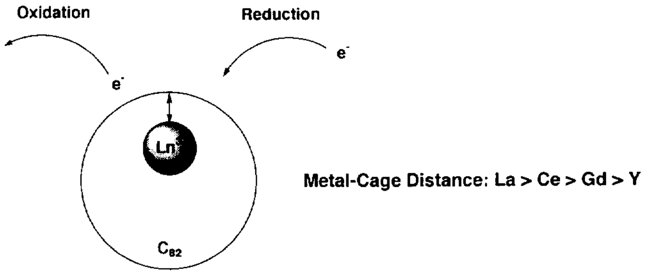

Figure 7. Relationship between the metal-cage distances and the redox potentials.

CONCLUSIONS

We have shown the first voltammograms of the pure fullerenolanthanides, La@C_{82}, Y@C_{82}, Ce@C_{82}, and Gd@C_{82}. The oxidation state of Ln@C_{82} changes from 2+ to 5- or 6- in our experiments. The difference between the first oxidation and reduction potentials is very small, probably due to the open-shell electronic structure. The fullerenolanthanides studied in the present work are strong electron donors as well as strong electron acceptors compared to empty fullerenes such as C_{60}, C_{70}, C_{76}, C_{82}, and C_{86}. The electronic properties of Ce@C_{82} and Gd@C_{82} are very similar to that of La@C_{82} and Y@C_{82}, although Ce and Gd have 4f electrons. This suggests that these 4f electrons do not play an important role in fullerenolanthanide chemistry as seen in organic and inorganic lanthanide chemistry.[34,35]

The fullerenolanthanides are new kinds of organolanthanide compounds stabilized by the delocalization of the negative charges on the fullerene cages and the protection of the lanthanide metals by spherical carbon ligands. Because only microgram quantities of the materials are available, the electrochemistry is quite useful to characterize the fullerenolanthanides.

EXPERIMENTAL SECTION

The production and purification of Y@C_{82}, Ce@C_{82}, and Gd@C_{82} were essentially the same as reported for La@C_{82}.[16] The soot containing Ln@C_{82} was prepared by an arc heating of Ln_2O_3 and graphite composite rods with an Ln/C ratio 1:100. The polystyrene (JAIGEL Co., CS_2 eluant) and Buckyclucher I columns (Regis Co., toluene eluant) gave HPLC profiles similar to those of La@C_{82}.[16] The time-of-flight mass spectrum indicated that higher fullerenes, such as C_{84}, C_{86}, and C_{88}, were completely removed.

Cyclic (CV) and differential pulse voltammograms (DPV) were recorded on a BAS-100B/W electrochemical analyzer. A three-electrode configuration was used throughout. All measurements were performed at ambient temperature under an argon atmosphere in 0.1 M 1,2-dichlorobenzene solution of $(n\text{-Bu})_4NPF_6$. The concentration of the fullerenolanthanides was 10^{-4} M. IR compensation was employed throughout. A platinum working electrode (1-mm diameter) was polished with 0.05-µm alumina before measurements. A platinum wire was used as the counter electrode. The reference electrode was a Ag/0.01 M $AgNO_3$ electrode filled with 0.1 M $(n\text{-Bu})_4NClO_4$ in CH_3CN. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc^+) as the internal standard. CV: scan rate, 20 mV/s. DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s.

ACKNOWLEDGMENT

We would like to thank Prof. S. Nagase for useful discussions.

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(*Received* 21 *June* 1995)