Electrochemical Properties of La@C_{82}

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Smalley and collaborators showed 2 years ago that La@C_{82} can be produced by laser vaporization of graphite and lanthanum oxide and extracted by toluene.[1] The following year, Johnson et al. found that La@C_{82} is a radical species which exhibits the EPR hyperfine structure, suggesting that the formal oxidation state of lanthanum is 3+.[2] Although the structure of La@C_{82} is still unknown,[3] some theorists proposed that the lanthanum atom does not locate in the center of the cage but is strongly coordinated by carbon atoms inside the cage.[4] Recently, Kikuchi et al. succeeded in isolating La@C_{82} in pure form and obtained the electronic spectrum with expected low-energy absorptions which are absent in empty C_{82}.[5] To get further information of the electronic structure of La@C_{82}, we performed electrochemical measurements and report here unusual redox properties of La@C_{82} which significantly differ from those of empty fullerenes.

Cyclic voltammograms (CV), differential pulse voltammograms (DPV), and Osteryoung square wave voltammograms (OSWV) were recorded on a BAS-100B/W with a three-electrode configuration. Less than 0.5 mg of chromatographically purified La@C_{82} dissolved in 5 mL of *o*-dichlorobenzene to give a dark green solution.[5] We first looked at the oxidation because we expected a series of three sequential one-electron steps due to C_{82}^{3-}. The scan started at the rest potential (+64 mV vs Ag/$AgNO_3$ reference electrode) toward the positive direction. Two oxidation peaks at +320 and +1340 mV were observed by DPV, and the latter was irreversible by CV and OSWV (Figure 1 and Table 1).[6] The first reversible oxidation potential is approximately equal to that of ferrocene, indicating that La@C_{82} is a moderate electron donor and therefore an oxygen-stable molecule.[7,8]

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− (Figure 1). In addition, La@C_{82} is a stronger electron acceptor than empty fullerenes such as C_{60}, C_{70}, C_{76}, and C_{84}.[8,9] Another electrochemical feature of La@C_{82} is the fact that the six reversible couples appear to be arranged in sets of two (${}^{ox}E1$ and ${}^{red}E1$, ${}^{red}E2$ and ${}^{red}E3$, and ${}^{red}E4$ and ${}^{red}E5$), unlike those of empty fullerenes.[8,9]

Figure 2 shows a schematic energy diagram of La@C_{82}.[4b] 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 reason for the unique arrangement

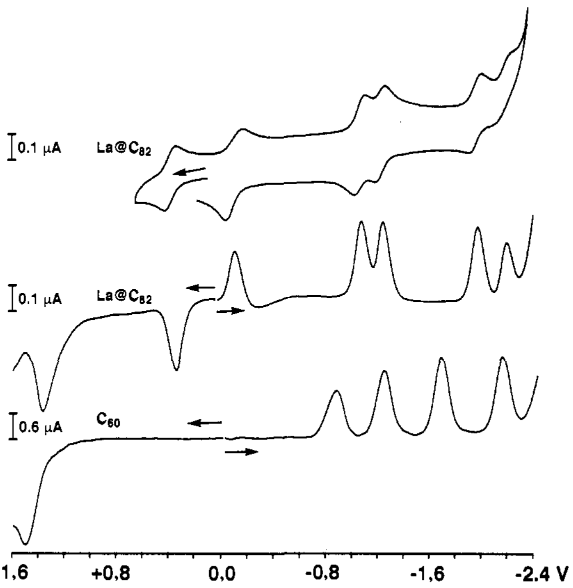

Figure 1. Cyclic voltammogram of La@C_{82} and differential pulse voltammograms of La@C_{82} and C_{60} in *o*-dichlorobenzene.

Table I. Half-Cell Potentials (CV, first row for each set of data) and Peak Potentials (DPV, second row; OSWV, third row) of La@C_{82}, C_{60}, C_{70}, and Ferrocene

${}^{ox}E2$	${}^{ox}E1$	${}^{red}E1$	${}^{red}E2$	${}^{red}E3$	${}^{red}E4$	${}^{red}E5$
			La@C_{82}			
b	+340	−154	−1103	−1260	−1991	*c*
+1340	+320	−124	−1084	−1256	−1972	−2192
d	+348	−160	−1120	−1288	−2032	−2260
			C_{60}			
	b	−857	−1233	−1685	*c*	
	+1484	−864	−1232	−1672	−2140	
	+1528	−896	−1264	−1704	−2172	
			C_{70}			
	b	−827	−1211	−1607	−2030	
	+1508	−856	−1212	−1608	−2016	
	+1512	−892	−1228	−1624	−2032	
			Ferrocene			
	+270					
	+276					
	+336					

[a] All potentials in mV. Conditions: working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M $AgNO_3$ and 0.1 M $(n\text{-}Bu)_4NClO_4$ in CH_3CN; supporting electrolyte, 0.1 M $(n\text{-}Bu)_4NPF_6$. CV: scan rate, 20 mV/s. DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s. OSWV: square wave amplitude, 25 mV; frequency, 15 Hz; step *E*, 4 mV; scan rate, 60 mV/s. [b] Irreversible. [c] Exact potentials were not determined due to the background current. [d] A broad peak at +1424 mV.

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[6] Even faster scan rates (up to 1000 mV/s) by CV did not improve the irreversibility of the second oxidation.

[7] Other lanthanum-containing fullerenes, such as La@C_{76}, La_2@C_{84}, and La@C_{82} isomers, turned out to be air-sensitive molecules. (a) Alverez, M. M.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Min, K. S.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 10561. (b) Suzuki, S.; Kawata, S.; Shiromaru, H.; Yamauchi, K.; Kikuchi, K.; Kato, T.; Achiba, Y. *J. Phys. Chem.* **1992**, *96*, 7159. (c) Hoinkis, M.; Yannoni, C. S.; Bethune, D. S.; Salem, J. R.; Johnson, R. D.; Crowder, M. S.; de Vries, M. S. *Chem. Phys. Lett.* **1992**, *198*, 461. (d) Bandow, S.; Kitagawa, H.; Mitani, T.; Inokuchi, H.; Saito, Y.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Shinohara, H. *J. Phys. Chem.* **1992**, *96*, 9609.

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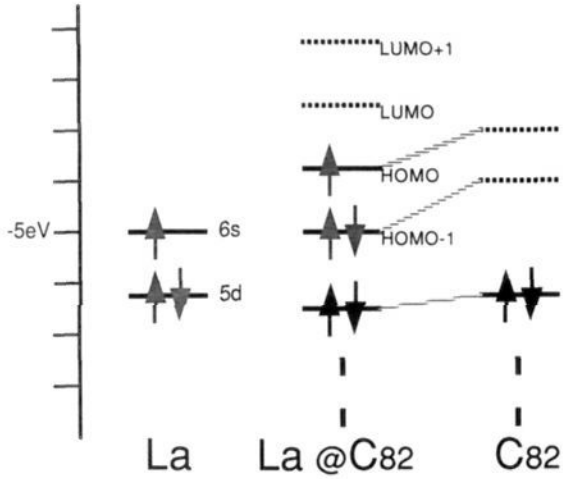

Figure 2. Schematic energy diagram of La@C_{82}.

of six reversible couples is not clear at this point. We speculate that this could be due to relatively large energy gaps of the HOMO–LUMO and LUMO–LUMO + 1 and small electron repulsion between electrons on those MOs.[4b] (4) Low-lying HOMO − 1 could be responsible for the irreversible formation of the di- or trication of La@C_{82} in our experiment. (5) The calculation on La@C_{82} showed that the LUMO and LUMO + 1 derive from the C_{82} MOs, not from 5d and 6s AOs of the lanthanum metal.[4b] We suggest that the reductions at least up to 5− are not metal-centered processes (i.e., La(III) to La(0)).

In conclusion, we have shown the first voltammograms of the pure metallofullerene La@C_{82}, which exhibits five reversible reduction and one reversible oxidation processes. The first *oxidation and reduction potentials indicate that it should form* both cationic and anionic charge-transfer complexes.[10] Physical properties of neutral and doped compounds are of great interest.

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(10) When La@C_{82} in *o*-dichlorobenzene was treated with I_2 and TCNQ, the EPR signals did not disappear. This preliminary result is consistent with the relative donor strength of La@C_{82} and suggests that even stronger acceptors will be needed to oxiidize this metallofullerene.