

The Voltammetry of $\text{Sc}_3@C_{82}$

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Many endohedral metallofullerenes have a C_{82} cage surrounding the metals, even though the normal arc-vaporization method of fullerene preparation does not generate C_{82} in significant abundance.^{1–10} Manolopoulos *et al.*^{11–13} attribute the low abundance of empty-cage C_{82} to the unfavorable electron configuration of this species. Consequently, the prevalence of C_{82} in metallofullerenes may be the result of an electron transfer from the encapsulated metal atoms to the fullerene cage.^{10–13} The extent of this charge transfer also contributes to the properties (e.g. catalytic, superconductive, nonlinear optical, and ferromagnetic) that are attributed to the endohedral metallofullerenes.^{14,15} Because of the importance of the charge transfer reaction, characterization of metallofullerenes by spectroscopy and electrochemistry is an active area of research.^{1–16} Only recently, however, have sufficient quantities of pure metallofullerenes and C_{82} been available for investigations of this type.^{3–5,16–20} Here, we report the square-wave voltammetry of $\text{Sc}_3@C_{82}$ in pyridine and find that it resembles that for $\text{La}@C_{82}$ and $\text{Y}@C_{82}$,^{3–5} but $\text{Sc}_3@C_{82}$ transfers more electrons to the cage than the monometallic endohedral metallofullerenes (MMF's).

(1) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Hauffler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* **1992**, *190*, 460–464.

(2) Shinohara, H.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Ohkouchi, M.; Ando, Y.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 4259–4261.

(3) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006–11007.

(4) Yamamoto, K.; Funasaka, H.; Takahashi, T.; Akasaka, T.; Suzuki, T.; Maruyama, Y. *J. Phys. Chem.* **1994**, *98*, 12831–12833.

(5) Kikuchi, K.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Suzuki, T.; Maruyama, Y. *J. Am. Chem. Soc.* **1994**, *116*, 9367–9368.

(6) Johnson, R. D.; de Vries, M. S.; Salem, J.; Bethune, D. S.; Yannoni, C. S. *Nature* **1992**, *355*, 239–240.

(7) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Honda, M.; Matsumiya, H.; Moriwaki, T.; Suzuki, S.; Shiromaru, H.; Saito, K.; Yamauchi, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1992**, *188*, 177–180.

(8) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142–145.

(9) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548–551.

(10) Nagase, S.; Kobayashi, K.; Kato, T.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *201*, 475–480.

(11) Manolopoulos, D. E.; Fowler, P. W. *Chem. Phys. Lett.* **1991**, *187*, 1–7.

(12) Fowler, P. W.; Manolopoulos, D. E. *Nature* **1992**, *355*, 428–430.

(13) Manolopoulos, D. E.; Fowler, P. W.; Ryan, R. P. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1225–1226.

(14) Beyers, R.; Kiang, C.-H.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Harich, K.; Stevenson, S. *Nature* **1994**, *370*, 196–199.

(15) van Loosdrecht, P. H. M.; Johnson, R. D.; de Vries, M. S.; Kiang, C.-H.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Stevenson, S. *Phys. Rev. Lett.* **1994**, *73*, 3415–3418.

(16) Burbank, P. M.; Gibson, J. R.; Dorn, H. C.; Anderson, M. R. *J. Electroanal. Chem.*, in press.

(17) Nagase, S.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1837–1838.

(18) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67–70.

(19) Stevenson, S.; Dorn, H. C.; Burbank, P.; Harich, K.; Haynes, J.; Kiang, C.-H.; Salem, J. R.; de Vries, M. S.; van Loosdrecht, P. H. M.; Johnson, R. D.; Yannoni, C. S.; Bethune, D. S. *Anal. Chem.* **1994**, *66*, 2675–2679.

(20) Stevenson, S.; Dorn, H. C.; Burbank, P.; Harich, K.; Sun, Z.; Kiang, C.-H.; Salem, J. R.; de Vries, M. S.; van Loosdrecht, P. H. M.; Johnson, R. D.; Yannoni, C. S.; Bethune, D. S. *Anal. Chem.* **1994**, *66*, 2680–2685.

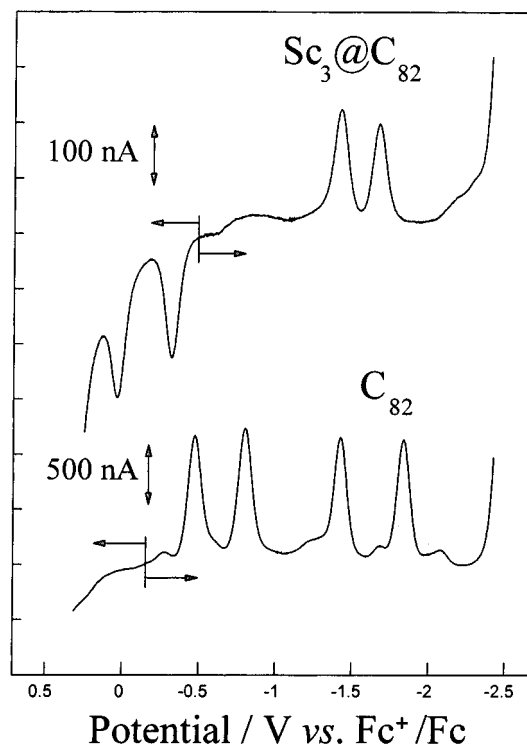


Figure 1. Square wave voltammograms of $\text{Sc}_3@C_{82}$ and C_{82} in pyridine containing 0.10 M $(n\text{-Bu})_4\text{NClO}_4$. Voltammetric data were collected using a frequency of 15 Hz, a peak amplitude of 25 mV, and a potential step size of 2 mV. Initial potentials were set at the open circuit potential values for both positive and negative scans. Limited sample size required using a micro-electrochemical cell containing 50 μL of the pyridine solution.¹⁶

Table 1. Redox Potentials versus Fc^+/Fc for C_{82} , $\text{Sc}_3@C_{82}$, $\text{La}@C_{82}$, and $\text{Y}@C_{82}$

| compd | oxE | oxE | oxE | redE | redE | redE | redE |
|------------------------|------|-------|-------|-------|-------|-------|-------|
| C_{82}^a | | | | -0.47 | -0.80 | -1.42 | -1.84 |
| $\text{Sc}_3@C_{82}^a$ | | -0.04 | -0.32 | | | -1.42 | -1.67 |
| $\text{La}@C_{82}^b$ | 1.07 | -0.07 | | -0.42 | | -1.37 | -2.26 |
| $\text{Y}@C_{82}^b$ | 1.07 | 0.10 | | -0.34 | | -1.34 | -2.22 |

^a The conditions for the voltammetry experiments are as follows: approximately 5×10^{-4} M of the fullerene in pyridine containing 0.10 M $(n\text{-Bu})_4\text{NClO}_4$, a glassy carbon working electrode, Pt wire counter electrode, and an Ag/Ag^+ reference electrode (potentials are converted to a Fc^+/Fc reference). ^b Reference 5.

The square-wave voltammetry of $\text{Sc}_3@C_{82}$ in pyridine containing 0.10 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ has two reversible oxidation peaks, two reversible reduction peaks, and two shoulders at potentials close to the solvent reduction (Figure 1, Table 1).²¹ The first oxidation peak (-0.32 V vs Fc^+/Fc) occurs at a potential negative of the oxidation of most fullerenes,²² and negative of the first oxidation of the C_{82} MMF's.^{3–5} The second oxidation (-0.04 V) of $\text{Sc}_3@C_{82}$ occurs at approximately the same potential as the first oxidation of the MMF's. Oxidation of $\text{Sc}_3@C_{82}$ occurs more easily than the oxidation of previously reported fullerenes, corresponding with the expectation that the Sc trimer transfers more electrons to the cage than the MMF's.

The oxidations of $\text{Sc}_3@C_{82}$ resemble the voltammetric behavior of the MMF's (Table 1). The first oxidation of $\text{Y}@C_{82}$ (0.10 V vs Fc^+/Fc) and of $\text{La}@C_{82}$ (-0.07 V) is at approximately the same potential as the second oxidation peak of $\text{Sc}_3@C_{82}$ (-0.04 V); however, the second oxidation of $\text{La}@C_{82}$

(21) $\text{Sc}_3@C_{82}$ was chromatographically purified as described in refs 19 and 20.

(22) Yang, Y.; Arias, R.; Eshegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801.

(1.07 V) and $Y@C_{82}$ (1.07 V) is at more positive potentials (at potentials outside of the available potential window for the pyridine solutions) than either of the $Sc_3@C_{82}$ oxidations. In addition, the second oxidations of $La@C_{82}$ and $Y@C_{82}$ are irreversible, while both oxidations of $Sc_3@C_{82}$ are reversible ($\Delta E_p \approx 70$ mV by cyclic voltammetry). The first oxidation of $Sc_3@C_{82}$ (-0.32 V) occurs at approximately the same potential as the first reduction of $Y@C_{82}$ (-0.34 V) and $La@C_{82}$ (-0.42 V). The correspondence between the oxidations of $Sc_3@C_{82}$ and the voltammetry of the MMF's suggests a relationship between the molecular orbital energies of these C_{82} endohedral metallofullerenes.

The first reduction peak of $Sc_3@C_{82}$, at -1.42 V, is negative of the first reduction of the MMF's, but is at approximately the same potential as the second reduction of $La@C_{82}$ (-1.37 V) and $Y@C_{82}$ (-1.34 V). The first reduction of $Sc_3@C_{82}$ is closely followed by the second reduction (-1.66 V). The second reduction of $La@C_{82}$ or $Y@C_{82}$ is either a simultaneous two-electron process or two closely spaced one-electron processes,³⁻⁵ similar to the appearance of the $Sc_3@C_{82}$ voltammogram (the potential difference between the $Sc_3@C_{82}$ reduction peaks is 0.24 V). Prior to the onset of solvent breakdown, two shoulders are found at potentials (-2.17 and -2.29 V) close to the values of the third and fourth reductions of the MMF's.⁴ These features are difficult to determine accurately due to the proximity of the electrolyte reduction. The negative potential of the initial reduction of $Sc_3@C_{82}$ correlates with the expectation that the Sc trimer transfers more electrons to the fullerene cage than the MMF's.

The correspondence of the voltammetry of $La@C_{82}$,^{3,4} $Y@C_{82}$,⁵ and $Sc_3@C_{82}$, as discussed above, implies that the molecular orbital energies of these C_{82} metallofullerenes are similar. Because the oxidation of $Sc_3@C_{82}$ at -0.32 V occurs at nearly the same potential as the first reduction of $La@C_{82}$ and $Y@C_{82}$, the Sc trimer appears to transfer one more electron to the cage than either La or Y during the metallofullerene formation. This interpretation of the voltammetry predicts, therefore, that the product of the first reduction of the MMF's, $La@C_{82}^-$ and $Y@C_{82}^-$, has the same open shell electron configuration as $Sc_3@C_{82}$. Consequently, $La@C_{82}^-$ and $Y@C_{82}^-$ should also be EPR active, as observed with $Sc_3@C_{82}$.²³⁻²⁷ Our interpretation of the $Sc_3@C_{82}$ electrochemistry is contrary to that of Suzuki *et al.*,³ who attribute the relative ease of the first reduction of the MMF's to the formation of a closed shell

electron configuration.³ Kadish *et al.*, however, show by combined electrochemistry and EPR spectroscopy that both C_{84}^- and C_{84}^{2-} are EPR active.^{28,29} Although not metallofullerenes, these C_{84} anions are isoelectronic with the C_{82}^{3-} and C_{82}^{4-} , the forms of C_{82} postulated for $La@C_{82}$ and $La@C_{82}^-$.¹⁰

The potential of the first reduction of $Sc_3@C_{82}$ and the potential of the third reduction of C_{82} are nearly identical. Ungerer and Hughbanks, using extended Hückel calculations, predict an MO diagram for $Sc_3@C_{82}$ in which two electrons are transferred from the Sc_3 cluster to the C_{82} cage.³⁰ In their MO diagram, a low lying SOMO for the metallofullerene has approximately the same energy as the LUMO for C_{82}^{2-} . These MO diagrams suggest that the first reduction of $Sc_3@C_{82}$ occurs at nearly the same potential as the reduction of C_{82}^{2-} to C_{82}^{3-} , as observed experimentally (Figure 1). A two-electron charge transfer by the Sc trimer to the cage, however, does not correspond with our interpretation that the formal charge of the Sc trimer is +4 (by analogy to the expected +3 charge for La and Y in the monometallic compounds, and the assumption that each redox process observed in the $Sc_3@C_{82}$ voltammetry involves transfer of only one electron).^{1,3-6} Smalley *et al.* suggest that, for $La@C_{82}$, two electrons are transferred to the π orbitals of the fullerene cage forming the stable C_{82}^{2-} , and the third electron is delocalized within the carbon cage.¹ The similarity of the voltammetry for $Sc_3@C_{82}$, C_{82} , and $La@C_{82}$ suggests that formation of $Sc_3@C_{82}$ may also result from delocalization of some of the transferred electron density within the cage instead of complete transfer of all four electrons to the π orbitals of the cage. Delocalized electrons within the cage might also explain the equivalence of the encapsulated Sc trimer.²²⁻²⁵ A necessary caveat for comparison of the MMF's and $Sc_3@C_{82}$ voltammetry with that of the empty-cage C_{82} is that all of these fullerenes have the same cage symmetry.²⁹

In summary, we have described the first electrochemical data for a polymetallic endohedral metallofullerene. The voltammetric behavior of $Sc_3@C_{82}$ resembles that for $La@C_{82}$ and $Y@C_{82}$,³⁻⁵ indicating that the identity of the metal does not influence dramatically the energies of the metallofullerene molecular orbitals.³¹ The three Sc atoms, however, transfer more electrons from the encapsulated metals to the cage than the monometallic counterparts, accounting for the differences in the voltammetry for $Sc_3@C_{82}$. The similarity of the voltammetry of $Sc_3@C_{82}$ with that of the MMF's suggests that $Sc_3^{+4}@C_{82}^{4-}$ may describe the formal charges on the Sc trimer and the C_{82} cage of this species. Metallofullerene electronic structure and physical properties should be better understood as more new metallofullerenes become available for investigation.

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(23) Kato, T.; Bandou, S.; Inakuma, M.; Shinohara, H. *J. Phys. Chem.* **1995**, *99*, 856-858.

(24) Suzuki, S.; Kojima, Y.; Nakao, Y.; Wakabayashi, T.; Kawata, S.; Kikuchi, K.; Achiba, Y.; Kato, T. *Chem. Phys. Lett.* **1994**, *229*, 512-516.

(25) Kato, T.; Bandou, S.; Inakuma, M.; Shinohara, H.; Hayashi, N.; Saito, Y. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Proceeding Series; Electrochemical Society: Pennington, NJ, 1994; pp 1331-1339.

(26) Shinohara, H.; Kishida, M.; Nakame, T.; Kato, T.; Bandou, S.; Saito, Y.; Wang, W. D.; Hashizume, T.; Sakurai, T. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Proceeding Series; Electrochemical Society: Pennington, NJ, 1994; pp 1361-1381.

(27) Yannoni, C. S.; Hoinkis, M.; de Vries, M. S.; Bethune, D. S.; Salem, J. R.; Crowder, M. S.; Johnson, R. D. *Science* **1992**, *256*, 1191-1192.

(28) Boulas, P. L.; Jones, M. T.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R.; Tse, D. S.; Kadish, K. M. *J. Phys. Chem.* **1996**, *100*, 7573-7579.

(29) Boulas, P.; Jones, M. T.; Kadish, K. M.; Ruoff, R. S.; Lorents, D. C.; Tse, D. S. *J. Am. Chem. Soc.* **1994**, *116*, 9393-9394.

(30) Ungerer, J. R.; Hughbanks, T. *J. Am. Chem. Soc.* **1993**, *115*, 2054-2055.

(31) The electrochemistry of $Sc@C_{82}$ has not been reported; however, Yannoni *et al.* report that the EPR spectrum of $Sc@C_{82}$ is similar to that of $La@C_{82}$, suggesting that these species have similar electronic ground state structures (ref 27).