Electrochemical Detection of C_{60}^{6-} at Low Temperature

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Low temperature cyclic voltammetry (CV) in water-free *N,N*-dimethylformamide (DMF)–toluene (2:3) mixture containing 0.1 mol dm^{-3} tetraethylammonium hexafluorophosphate (TEAH) showed a complete set of six one-electron reversible waves for C_{60}, providing evidence for the existence of C_{60}^{6-}.

According to recent electrochemical studies,[1–4] C_{60} is irreversibly oxidized and reversibly reduced. The study by Dubois *et al.*[4] demonstrated five reversible reduction waves of this molecule, *i.e.* reversible generation of C_{60}^{5-}. To overcome the solubility problem of C_{60} the measurements were made in benzene containing $[(n\text{-}C_6H_{13})_4N](ClO_4)$ at 45 °C. As this highly symmetrical C_{60} molecule (I_h symmetry[5]) has threefold degenerate LUMOs,[6–9] it is expected that cyclic voltammetry for C_{60} would exhibit six one-electron reduction waves if sufficiently negative potentials are covered. In low temperature CV, the usable potential window is wider, particularly in the negative direction,[10,11] and a reduced state is generally more stable at low temperatures. This communication deals with the first electrochemical detection of C_{60}^{6-} in solution by low temperature CV.

To carry out low temperature CV for C_{60}, mixtures of DMF–toluene were successfully used. Distilled toluene was dried over sodium metal for several days and, prior to use, vacuum distilled into an air-tight electrolysis cell with supporting electrolyte and C_{60}. Into the electrolysis cell, dry DMF was vacuum distilled from a sodium anthracenide solution of DMF,[11] the initial about 10% being discarded. Without this procedure, the first reduction wave of C_{60} was depressed, probably owing to some kind of interaction between C_{60} and an unknown decomposition product. The ferrocenium/ferrocene redox couple ($Fc^{+/0}$) was used as an internal potential reference. An ethanol-bath cooled by liquid nitrogen was used. Other experimental details are similar to those described elsewhere.[11]

CV for C_{60} in 0.1 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate (TBAH) in DMF–toluene (volume ratio = 1:1) mixture at −60 °C showed five well-defined reversible reduction waves and an indication of a sixth wave. The sixth wave is probably overlapped by suddenly rising background current, which is characteristic of the negative potential limit under our experimental conditions. To clarify the presence of the sixth reduction wave, the ion-association of highly reduced C_{60} with tetraalkylammonium cations, by which the sixth wave

Table 1 Cyclic voltammetric data obtained with 0.3 mmol dm^{-3} C_{60} DMF–toluene solutions at low temperature

	($E_{1/2}{}^{a}$ *vs.* Fc$^{+/0}$)/V						
Supporting electrolyte	0/−	−/2−	2−/3−	3−/4−	4−/5−	5−/6−	$E_{\text{limit}}{}^{b}$
0.1 mol dm^{-3} TEAH DMF–toluene (2:3) at −88 °C	−0.81	−1.24	−1.77	−2.22	−2.71	−3.12	−3.5
0.1 mol dm^{-3} TBAH DMF–toluene (1:1) at −60 °C	−0.82	−1.26	−1.82	−2.33	−2.89	−3.34^{c}	−3.5

^{a} $E_{1/2}$: midpoint potential. ^{b} E_{limit}: cathodic potential limit. ^{c} Anodic peak potential.

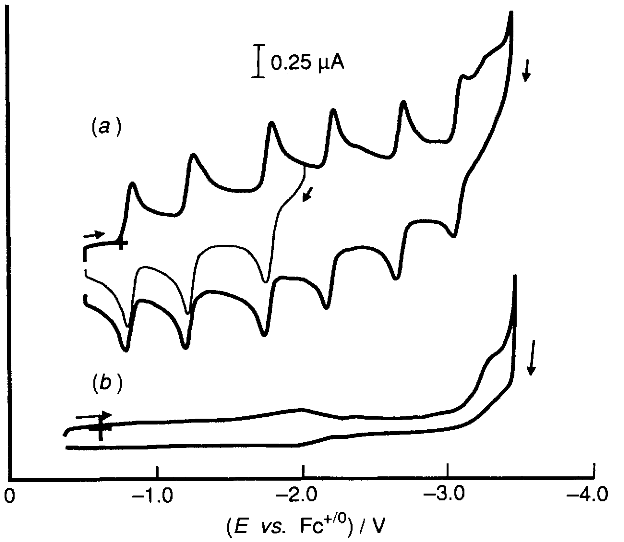

Fig. 1 (*a*) Typical cyclic voltammograms with 0.3 mmol dm^{-3} C_{60} in DMF–toluene (2:3) containing 0.1 mol dm^{-3} TEAH at −88 °C. (*b*) The corresponding background current in the absence of C_{60}. A scan rate of 30 mV s^{-1} was used. A platinum wire working electrode of *ca.* 0.08 cm^{2} area was used.

might shift towards a less negative direction, was taken into account. As smaller tetraethylammonium cations associate with negative ions more strongly than larger tetra-n-butylammonium cations,[11] the use of TEAH should cause a positive shift in the redox potential of the sixth wave. Fig. 1(*a*) gives typical cyclic voltammograms of C_{60} in DMF–toluene (volume ratio = 2:3) mixture with 0.1 mol dm^{-3} TEAH at −88 °C. A complete set of six waves is clearly shown in this figure, although the sixth wave is partly overlapped by the background current, which is given in Fig. 1(*b*). The first four reduction steps have been concluded to be one-electron reversible steps.[3] The peak in the negative-direction scan in each step and the corresponding one in the positive-direction scan were nearly equal in height and separated by about 50 mV. The deviation of the peak separation from the theoretical value of 36 mV for a one-electron reversible wave at −88 °C is probably due to the uncompensated solution resistance. Therefore, it can be concluded that these six waves are all reversible one-electron steps, and our results provide evidence for the existence of $C_{60}{}^{6-}$. At −88 °C, the sample solutions were in a supercooled state. After 20–30 min the deposition of the supporting electrolyte was observed. All CV measurements at −88 °C were made before the deposition of the supporting electrolyte. Table 1 lists the midpoint potential ($E_{1/2}$) between the cathodic and the anodic peak potential for each reduction step obtained with a 0.3 mmol dm^{-3} solution of C_{60} in DMF–toluene with either 0.1 mol dm^{-3} TEAH or 0.1 mol dm^{-3} TBAH. The midpoint potential can be identified by the half-wave potential.

As demonstrated in this study, low temperature CV might be an important method for studying fullerenes, metal ion-including fullerenes, hydrogenated fullerenes, and other fullerene-related compounds.

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