

## Electrochemical Generation of $C_{60}^{2+}$ and $C_{60}^{3+}$

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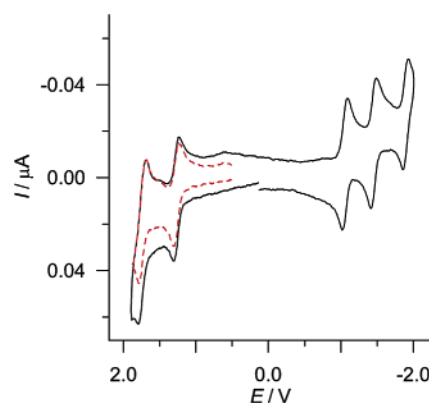
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The facile reduction of fullerenes, exemplified by the electrochemical stepwise reversible addition of up to six electrons to  $C_{60}$  and  $C_{70}$ ,<sup>1</sup> contrasts with their difficult oxidation.<sup>2</sup> Furthermore, in condensed media, fullerene radical cations, the first all-carbon carbocations, react immediately with any nucleophile present in solution, leading to decomposition.<sup>2</sup> This was observed in early CV experiments with the generation of multielectron oxidation peaks, as the decomposition products undergo further oxidation.<sup>3</sup> In 1993, Echegoyen et al., employing scrupulously dried tetrachloroethane (TCE), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte, and low temperatures, reported the first observation of electrochemical reversible one-electron oxidation of  $C_{60}$  at  $E_{1/2} = 1.26$  V (vs Fc<sup>+/0</sup>).<sup>4</sup> Transient production of  $C_{60}^+$  in solution was also obtained photochemically<sup>2,5</sup> and by pulse radiolysis.<sup>6</sup> Superacidic conditions were used to stabilize either chemically or electrochemically generated  $C_{60}^+$ ,<sup>7</sup> while the preparation of stable solutions of  $C_{60}^+$  was achieved by using triarylammonium radical cation with a carborane counteranion,<sup>8a</sup> i.e., an oxidant that is strong enough to oxidize the fullerene without bringing along a reacting nucleophilic anion. Very recently, C<sub>59</sub>N<sup>+</sup> carbocation was also obtained by exploiting the very low nucleophilicity of carboranes.<sup>8b</sup>

Higher fullerenes are easier to oxidize than  $C_{60}$ , and the second electrochemical oxidation (although irreversible) of  $C_{70}$ ,  $C_{76}$ , and  $C_{78}$  in TCE/TBAPF<sub>6</sub> was reported.<sup>2</sup> By contrast, the further oxidation of  $C_{60}^+$  was disallowed likely by the narrowness of the positive potential window available in such a solvent.<sup>4</sup> Furthermore,  $C_{60}^{2+}$  is an exceedingly reactive species,<sup>2,8a</sup> and evidence of formation of  $C_{60}^{2+}$  in condensed media has so far been reported only in intercalation compounds, obtained by reacting AsF<sub>5</sub> and SbF<sub>5</sub> with solid  $C_{60}$  in liquid SO<sub>2</sub>, where the resulting solid was described as  $C_{60}(AsF_6)_2$  and  $C_{60}(SbF_6)_2$ , respectively.<sup>9</sup>

In the present work, we report for the first time on the cyclic voltammetric reversible generation of  $C_{60}^{2+}$  and  $C_{60}^{3+}$ . This was allowed by the adoption of suitable experimental conditions that comprise ultra-dry solvents and electrolytes with very high oxidation resistance and low nucleophilicity. Our experiments were carried out using as solvent dichloromethane (DCM) that, in contrast to liquid SO<sub>2</sub>, is widely used in fullerene electrochemistry.<sup>2,10</sup> Supporting electrolytes containing nucleophilic counteranions such as ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and, to a lesser extent, PF<sub>6</sub><sup>-</sup>, are known to attack  $C_{60}^+$  in such a solvent<sup>2c</sup> and were therefore avoided. On the other hand, AsF<sub>6</sub><sup>-</sup> is known for its high oxidation resistance and low nucleophilicity: TBAAsF<sub>6</sub> has been long used as a supporting electrolyte in liquid SO<sub>2</sub> where it allowed electrochemical investigations at potentials as high as 4.7 V (vs SCE) and the observation of several reacting radical cations.<sup>11</sup> As a matter of fact, the very low nucleophilicity of AsF<sub>6</sub><sup>-</sup> was confirmed in the present case by



**Figure 1.** Cyclic voltammetric curves of a 0.15 mM (saturated)  $C_{60}$ , 0.05 M TBAAsF<sub>6</sub> DCM solution. Working electrode: Pt disk (125  $\mu$ m diameter). Scan rate: 1 V/s.  $T = 25$  °C. Red curve: as black curve after background current correction.

carrying out the CV experiments in a saturated  $C_{60}$  (0.15 mM) DCM solution, with 0.05 M TBAAsF<sub>6</sub> as a supporting electrolyte. The CV curve displayed in Figure 1 obtained at 25 °C and 1 V/s shows, along with three reversible one-electron reduction peaks at  $-1.06$ ,  $-1.46$ , and  $-1.89$  V ( $E_{1/2}$  values vs Fc<sup>+/0</sup>), two reversible one-electron oxidation peaks with  $E_{1/2} = 1.27$  and  $1.71$  V that were attributed to the subsequent oxidations of  $C_{60}$  to  $C_{60}^+$  and  $C_{60}^{2+}$ , respectively, the latter, to the best of our knowledge, for the first time detected in solution. All peaks display (after correction for the background current) similar heights, reverse-to-forward peak separations within 100 mV (Table 1), and reverse-to-forward peak height ratios  $\sim 1$ , as expected for chemically and electrochemically reversible processes.<sup>12</sup>

$C_{60}^+$  and  $C_{60}$  anions are rather stable species under the conditions of Figure 1 as was demonstrated by the invariance of the CV morphology upon repeatedly scanning potential between  $-1.8$  and  $1.6$  V (Figure S1, Supporting Information). Conversely, when the second oxidation peak is included in the repetitive potential scan, the partial degradation of  $C_{60}^{2+}$  is observed yielding some electroactive material, in turn responsible for novel irreversible reduction peaks appearing in the reverse scan at  $0.6$  and  $1.5$  V and leading to rapid electrode fouling.<sup>13</sup> Such peaks are already observed, although with very low intensities, in the first scan shown in Figure 1. This indicates that  $C_{60}^{2+}$  is a very unstable species even in the conditions adopted here with an estimated lifetime  $\leq 100$  ms. However, the use of low temperatures and higher scan rates (using an ultramicroelectrode) greatly stabilized the dication and allowed observation of a further reversible oxidation peak at more positive potentials, which was reasonably attributed to the generation of  $C_{60}^{3+}$ . Figure 2 shows the CV curve obtained at  $-55$  °C and 100 V/s, where the anodic peaks, all displaying a cathodic counterpart, were attributed to three subsequent one-electron oxidations of  $C_{60}$ , with  $E_{1/2} = 1.27$ ,  $1.71$ , and  $2.14$  V, respectively. Not unexpectedly,

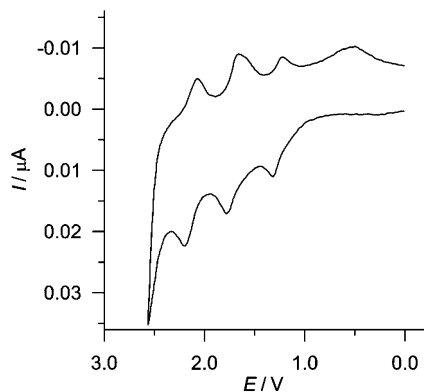
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**Table 1.** Halfwave Potentials ( $E_{1/2}/V$ , vs  $Fc^+/Fc$ ) and Corresponding Peak Separation (in Parentheses, mV) of Oxidations and Reductions of  $C_{60}$  in Various Media<sup>a</sup>

solvent/supporting electrolyte	oxidations			reductions		
	I	II	III	I	II	III
DCM/TBAAsF <sub>6</sub>	1.27 (70)	1.74 (91)	2.14 (139) <sup>b</sup>	-1.06 (68)	-1.46 (72)	-1.89 (69)
TCE/TBAPF <sub>6</sub>	1.26 (79)			-1.08 (78)	-1.45 (75)	
DCM/TBATFAB	1.23 (70)			-1.11 (74)	-1.49 (70)	-1.93 (82)

<sup>a</sup>  $T = 25\text{ }^\circ\text{C}$ . Scan rate = 1 V/s. Working electrode: Pt disk (diameter: 125  $\mu\text{M}$ ). <sup>b</sup>  $T = -55\text{ }^\circ\text{C}$ . Scan rate = 100 V/s. Working electrode: Pt disk (diameter: 25  $\mu\text{M}$ ).



**Figure 2.** Cyclic voltammetric curve (after background current correction) of a 0.15 mM (saturated)  $C_{60}$ , 0.05 M TBAAsF<sub>6</sub> DCM solution. Working electrode: Pt disk (diameter: 25  $\mu\text{m}$ ). Scan rate: 100 V/s.  $T = -55\text{ }^\circ\text{C}$ .

evidence of chemical degradation of highly oxidized  $C_{60}$  is observed in the reverse scan, as the reduction peak associated with the first oxidation is lower than expected and the irreversible peak at 0.6 V is significantly increased.<sup>13</sup> Remarkably, the potential separation between the subsequent oxidation processes matches that observed between the subsequent reductions in the same medium (Figure S2, Supporting Information, and Table 1), confirming the molecular capacitance behavior already observed in the cathodic charging of  $C_{60}$ .<sup>14</sup>

Finally, attempts to observe the reversible oxidation of  $C_{60}$  to the di- and trication using TBATFAB (TFAB =  $[B(C_6F_5)_4]^-$ ) as a supporting electrolyte failed. TFAB recently emerged as a very promising anion capable of stabilizing electrochemically generated and very electrophilic cations.<sup>15</sup> As a matter of fact,  $C_{60}^+$  proved to be stable in the CV time scale in DCM/TBATFAB solutions but, due to the limited oxidation resistance of the TFAB anion, higher oxidation states were not observed (Figure S3, Supporting Information, and Table 1). Analogous results were obtained in TCE with either TBAAsF<sub>6</sub> or TBATFAB as supporting electrolytes: in both cases, the one-electron reversible oxidation of  $C_{60}$  was obtained but the narrow positive potential window did not allow the detection of its higher redox states.

In conclusion, the DCM/TBAAsF<sub>6</sub> system is an ideal environment for the electrochemical investigation on  $C_{60}$  cations, allowing the detection of up to the trication. Both the solvent and the supporting electrolyte are readily available and purified by standard procedures. The present study adds valuable information on the still relatively unknown properties of positive redox states of  $C_{60}$  and, in view of the very high reactivity of higher cations,<sup>2d</sup> offers new possible routes for fullerene functionalization.

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**Supporting Information Available:** Experimental details, CV curves of  $C_{60}$  in DCM/TBAAsF<sub>6</sub>, TCE/TBAPF<sub>6</sub>, and DCM/TBATFAB, and a plot of halfwave potentials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Work is in progress aimed at the identification of the decomposition products of highly oxidized  $C_{60}$ . In the absence of other nucleophiles,  $C_{60}$  itself might be involved in the nucleophilic attack<sup>2d</sup> to  $C_{60}^{2+}$  (and  $C_{60}^{3+}$ ) (father–son reaction), thus leading to the formation of dimers and, possibly, oligomers in turn responsible for the observed electrode fouling.
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