

# ELECTROCHEMICAL METHOD FOR SYNTHESIS OF FULLERENE-CONTAINING COMPOUNDS AND COATING

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## ABSTRACT

The paper represents research into electrochemical properties of fullerenes. There exists principle possibility to produce coating of fullerenes and fullerene-containing products from their solutions by electrochemical technique what may widen application of this allotropic form of carbon as individual compounds as well as coating.

## INTRODUCTION

Availability of methods for producing fullerenes makes possible expansion of research into their physical and chemical properties.

C<sub>60</sub> fullerene is  $\pi$ -acceptor of the new type and has a number of significant features compared to other acceptor molecules: larger size, spherical form, unique electron structure, high symmetry and polarizability. These features introduce some specificity into donor-acceptor interaction in C<sub>60</sub> fullerene compounds. Fullerene is rather weak acceptor. Adiabatic affinity to an electron in the solution is 2.1-2.2 eV [1]. C<sub>60</sub> fullerene molecule can accept up to 12 electrons [1-4] and donates one electron [5], i.e. the charge on the C<sub>60</sub> molecule can change from +1 to -12. Polarizability of C<sub>60</sub> fullerene molecule is high ( $\alpha \sim 85 \text{ \AA}^3$ ), several times greater than that of other  $\pi$ -acceptor molecules. Therefore polarization Van der Waal forces play an important part in forming donor-acceptor complexes and ion-radicals salts of fullerenes.

According to the electrochemical method, C<sub>60</sub> anion-radicals are prepared by reducing neutral fullerenes on the platinum cathode. No polar solvents with high polarizability ( $\alpha \sim 10-20 \text{ \AA}^3$ ), especially derivatives of benzene: dichlorobenzene, toluene or their mixtures with dichloromethane, tetrahydrofurane showing higher dielectric permeability are used as solvents. Compounds with exchange cations are used as base electrolytes.

Two successive waves of reduction are described in the most of papers related to the research into electrochemical behavior of C<sub>60</sub>. However, different systems of solvents, base electrolytes and reference electrodes used in research give rise to the significant difference in the values of redox potentials. For C<sub>60</sub>/C<sub>60</sub><sup>-</sup> and C<sub>60</sub><sup>-</sup>/C<sub>60</sub><sup>-2</sup> pairs the redox potentials are -0.44 V and -0.82 V, respectively, in dichloromethane and acetonitrile [1,5] relative to the saturated calomel electrode (s.c.e.). The change of solvent polarizability somewhat shifts the redox potential of C<sub>60</sub>/C<sub>60</sub><sup>-</sup> pair. It equals -0.36 V and -0.33 V in benzene and tetrahydrofurane, respectively, relative to s.c.e.[6]. The values of -0.61 V and -1.00 V for the first and second redox potentials relative to s.c.e. [7] were obtained in methylene chloride. Three redox potentials for C<sub>60</sub> fullerene with the charge on the molecule from -1 to -3 were obtained in [8]. The values of -0.79V, -1.30V and -1.83V for three stages of reduction were obtained in the dimethylformamide-toluene mixture. When toluene was replaced by o-dichlorobenzene, the cathode shifts of redox potentials to -0.96 V, -1.41 V and -1.91 V were observed.

Fullerenes, especially C<sub>60</sub>, have high oxidation potentials. The oxidation potential of C<sub>60</sub> equal to +1.26 V relative to the ferrocene/ferrocene standard is given

in [9]. However, the data on existing individual compounds in which C<sub>60</sub> has positive charge are not available.

## EXPERIMENTAL TECHNIQUE

Electrodeposition of fullerenes was carried out using the two-electrode cell with Ni-electrodes 35x100 mm in size; the working part of the electrode was 10x10 mm in size. The specially designed potentiostat was used as dc source. It allowed the change of potential difference at the electrodes from 0 to 2000 V and the measurement of current intensities to 1 mA. The working volume of the cell corresponded to 30 ml. Electrolyte was fullerene solution in toluene of certain concentration with base electrolyte added into it.

Electrodeposition of fullerene films was carried out at room temperature and practically constant current density (0.4-0.6  $\mu\text{A}/\text{cm}^2$ ). Electrodes were preliminary subjected to mechanical polishing by chromium oxide and degreasing by organic solvents.

## RESULTS AND DISCUSSION

In selecting electrolyte the dielectric permeability of solvent need to be paid attention as its too low value gives rise to very high electrical resistance of the cell. The dielectric permeability of toluene equals  $\epsilon \approx 2.7$  and its electric conductivity practically equals zero. The same concerns the fullerene solution in toluene. In experiment we used ethanol as active additive to the solution to prepare conducting toluene and conducting fullerene solution in toluene.

Dielectric permeability of ethanol is rather high ( $\epsilon \approx 243$ ). Ethanol is easily mixed with toluene, do not react with fullerene, it is amphoteric solvent. Toluene-ethanol solution (TE) is rather good electrolyte and may be used for research into electrochemical properties of fullerenes as well as for their electrodeposition as coating or large amount of fullerene-containing or fullerene-derivative product on the electrodes.

Fig.1 shows current intensities versus potential difference at electrodes for TE and TFE solutions (curves 1 and 2, respectively). Fullerene concentration in TFE solution was 2.55 mg/ml. In both solutions the volume of ethanol additive was equal the toluene volume (1:1). As Fig.1 shows, fullerenes present in the solution cause some change of volt-ampere characteristic compared to that for TE-solution. In the range of potentials measured this characteristic becomes practically linear. In other equal conditions current intensities are somewhat lower than those in TE-solution. In

this case, using relation  $\frac{\Delta U}{\Delta I}$ , we may evaluate electric resistance of the cell. In our case resistance equals  $\approx 2.9 \cdot 10^5 \Omega$ . As the electrolyte composition changes, the value of electric resistance also changes. In time (in 3-4 h) curve 2 (Fig.1) presents linear dependence with two slopes. The value of  $\frac{\Delta U}{\Delta I} \approx 9 \cdot 10^5 \Omega$  corresponds to the low-voltage section (0-200 V) and  $\frac{\Delta U}{\Delta I} \approx 1.5 \cdot 10^6 \Omega$  corresponds to the high-voltage section (200-1200 V).

The value of current intensity depends not only on the potential difference at the electrodes, but also on the ethanol concentration in corresponding solutions. Fig.2 shows current intensities versus ethanol concentration in TE-solution for two values of voltage at the electrodes: 100 and 200 V. As Fig.2 shows, electric conductivity of TE-solution is built up with increasing ethanol concentration in it. The higher ethanol concentration is, the quicker conductivity is built up. Analogous concentration dependence is also found for TFE-solution. For electrodeposition of fullerene-containing products the ethanol concentration by volume was chosen in the range of 37 ÷ 50 wt.% to achieve acceptable electric conductivity of the solution.

Fig.3 shows chronometrical dependence  $I(t)$  for TE and TFE solutions (curves 1, 2, respectively) at working voltage at the electrodes  $U = 200$  V and approximately equal ethanol concentrations in the solutions. Significant change of current intensity is observed at the beginning of the experiment (0-20 min), further current intensity does not practically change (3-4 h), and then it is dropping slowly. Dependence  $I(t)$  is given for TE- and TFE-solutions aged for 24 h after their preparation.

On both electrodes we obtained fullerene-containing product from TFE-solution. Depending on the process conditions and the electrolyte composition, fullerene-containing product may be prepared at lower voltage ( $\approx 100$  V) at the electrodes as well as at higher voltage (800 V and higher).

Note that fullerene-containing products are simultaneously formed on the positive electrode (A) and the negative one (K). As this takes place, they are distinguished by composition, structure, adhesion and other physical and chemical properties.

Product forming on the anode is dense, with high adhesion, with slight regular reflection, consist of fullerites with FCC lattice, dissolve (very slowly) in toluene.

The coating forming on the cathode is friable; easily falls down (it may be removed by a brush). It is thicker than that on the anode, spongy, does not dissolve in toluene, its composition is of fullerene-compounds with hydrocarbons or their mixtures.

Structures of these films are given in Fig.4: a - anode film forming at 200 V, b - cathode film.

The structure of anode films consists of small crystals of cubic form. The structure of cathode films is spongy, cracked, consists of spherical particles.

## THERMOGRAVIMETRIC RESEARCH IN PRODUCT OF SYNTHESIS

Thermal decomposition of cathode and anode coating on Ni resulting from heating from room temperature to 800 °C was studied using Q-1500D derivatograph.

When heated in the temperature range of 200-300 °C, the cathode coating loses its mass rather intensively. At 300-550 °C the coating mass changes slightly. It is increased beginning from 500 °C (Fig.5, a) what results from oxidation of Ni foil at the temperature above 550 °C.

When heated to 600 °C, the very thin anode coating gains its mass. The anode coating completely disappears, slow oxidation of the support proceeds on the surface of Ni foil.

Fig.6 shows morphology of the nickel support surface (cathode) coated with the synthesis product. Fig.6 a,b,c – after annealing to 400 °C in air; Fig.6 d,e,f – after annealing to 800 °C

When subjected to thermotreatment in air, the product forming on both electrodes shows certain changes. After heating to 500 °C, the anode product is completely sublimated or oxidized by oxygen from air. At 200-300 °C the processes accompanied by significant mass losses and graphitization of the residue proceed in the cathode product. At 400 °C SEM shows aggregates of crystals with a regular form characteristic of fullerites on the electrode surface. However, the same crystals remain after annealing to 800 °C.

As in these processes fullerenes are the main carrier of a large amount of carbon, it would be correct to suppose that in thermotreatment of the cathode product its graphitization is catalyzed rather than decomposition of fullerene-containing product into fullerenes and residue followed by fullerene sublimation, like in thermotreatment of the anode. As the cathode product is not completely oxidized in air at 800 °C, it can be reasoned with certainty that in thermotreatment to 800 °C the graphite-like residue is formed.

The product formed in electrolysis of toluene-fullerene-ethyl alcohol solutions (TFE) on the anode and the cathode have been analyzed using Auger spectroscopy of high-energy resolution on Jet-10 apparatus and DRON-2 apparatus for XRD analysis in  $\text{CuK}_\alpha$  radiation according to the standard methods.

a) XRD research into the product of synthesis

The obtained diffractograms of anode and cathode product reveal the presence of fullerites. However, the anode diffractograms show the reflection lines corresponding only to FCC lattice of C<sub>60</sub>, and the cathode ones show strong reflection lines corresponding to FCC as well as HCP lattices of C<sub>60</sub> (Table 1)

Thus, the studied samples show superposition of two phases with C<sub>60</sub> FCC lattice predominating.

Diffractograms for both samples have halo in the angle range of  $2\theta=13^\circ - 20^\circ$ . The halo seems to correspond to the non-crystallized part of fullerites (or to the fullerites in the nanodispersed state) or to the fullerene-organic compounds.

b) Fig.7 shows results of layer-by-layer Auger spectral analysis of the electrolysis product formed on the cathode (a) and the anode (b). Both groups of spectra feature the lines of free carbon (260-280 eV), oxygen (~500 eV) as nickel oxide and nickel itself through the whole thickness of the product. The detailed layer-by-layer analysis of the product on both electrodes has revealed that the form of carbon spectra are distinguished in depth what may testify that carbon is in the different electron states (i.e. forming chemical bonds) depending on the depth. The states may be caused by recharging carbon atoms under the action of the ion argon beam in etching.

## CONCLUSIONS

The technique proposed may be used to produce the fullerene compounds with different organic and inorganic compounds and substance by the electrochemical technique in the industry scale. Chemical composition of products will greatly depend on the type of hydrocarbon solvent and the chemical composition of base electrolyte as well as conditions of synthesis.

Moreover, this technique makes possible fullerene-containing coating that may be used as film coating for special application as well as intermediate product. Further thermal and thermo chemical treatment of this product may allow preparation either coating with original properties or coating consisting of products result from interaction between the fullerene-containing film and the support.

In the latter case the coating with certain chemical composition will be formed. This composition will smoothly turn into carbide (in the case of carbide-forming elements and compounds of the support) and then into the solid solution of carbon in the support. For example, the obtained surface will show tribological properties of fullerene and hardness of carbide and retain the unique chemical composition of the coating.

The technique proposed is highly promising for synthesis of fullerene-containing products as well as for processing the surface of hardware to provide them unique properties.

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