# CHEMICAL METHOD OF PRODUCING EXOFULLERENES IN SOLUTION

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## Introduction

Development of technological and reliable material with high capacity to storage hydrogen in its bound form will be an actual problem as before. Recent research into the use of fullerenes and carbon nanotubes has been much pursued for this purpose. It is appropriate to introduce a catalyst into the composition of material to gain a possibility to use mild conditions for hydrogen sorption-desorption during operation of the material. In this work we have considered a possibility of producing fullerenes with metal atoms added to a carbon molecule (exofullerenes) by a chemical method. This method consists in producing the solution of corresponding salts and conducting the reaction of metal ion reduction to the atomic state using specific reducers.

## Results and discussion

Nickel has been chosen as the metal precipitated because, firstly, it is a catalyst for the reaction of molecular hydrogen dissociation what is required for further applications of exofullerenes produced and, secondly, the reaction of its reduction is heterogeneous. This circumstance is a prerequisite to the production of nickel exofullerenes preferentially while, as an example, chemical reduction of copper ions gives a possibility of producing metal copper within the solution volume because the reaction of copper reduction proceeds according to the homogeneous mechanism. Centers of nickel crystallization (substrate) may be both different particles suspended in the solution and arrangements of molecules or individual large molecules. Hence from the theoretical point of view the application of the chemical method of reducing metal from solutions to produce nickel exofullerenes is well justified.

In practice the production of nickel exofullerenes is related to restrictions on the solubility of the most frequently used nickel salts, sulfates and chlorides, and different necessary additives and reducers in toluene because fullerenes in their molecular form exist only in the given solvent. Therefore two solutions have been prepared. The components required to conduct the reduction reaction have been dissolved in ethanol, fullerites have been dissolve in toluene. As fullerene are salted out from toluene by ethanol, one should expect some amounts of their crystalline form (fullerites) to form in the total solution. However under sufficiently intensive mechanical action (mixing the solution) there is a possibility of breaking up crystals as fullerene molecules are bound by weak Van der Waals forces in this solution.

| № 1 | № 2 |
|---|---|
| Toluene - 100 ml | $NiCl_26H_2$ - 3 g |
| Fullerites - 0.3 g | $NaCH_3COO$ - 2.5g |
| | $NaH_2PO_2$ - 4 g |
| | $C_2H_5OH$ - 0.5 *l* |

The formation of suspension has been observed during mixing solutions No 1 and No 2. The suspension has not been removed by filtration, i.e. fullerenes have been salted out partially. The reaction of nickel ion reduction occurs at an elevated temperature. Therefore the solution has been heated to 75$^o$C during the intensive mixing with a magnetic mixer. The reaction occurrence has been controlled by hydrogen evolution and the change of the solution color.

The reaction rate has been low and the full time of nickel precipitation has been 3 hours. After being dried, the formed friable precipitate is light-gray (Fig.1) while the initial fullerite powder was black.

Investigation into the composition of the prepared material using the X-ray microanalyzer SUPERPROBE-733 has been possible only on a compacted sample (Fig.2) as under an electron beam a dispersed sample was melt immediately. Investigation with characteristic radiation has shown dense and even nickel distribution on the whole area of the surface of the sample (Fig.3). Carbon distribution has been characterized by some large aggregates (Fig.4). This fact may be attributed to screening the substrate (fullerenes) by nickel on individual regions. TEM studies have confirmed this. A thick shell supposedly from nickel has been observed around individual aggregates of particles. The shell thickness has varied in a wide range but, as a rule, it has been observed around the aggregates (conglomerates) of particles. More detailed information on individual exofullerenes has not been possible to obtain using current equipment.

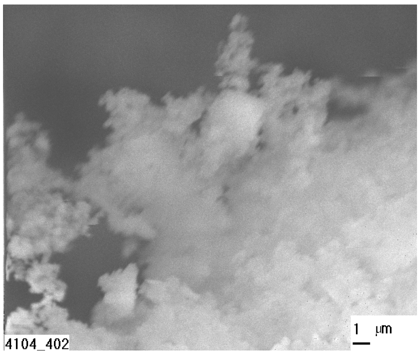

Fig.1. Nanoparticles coated with nickel

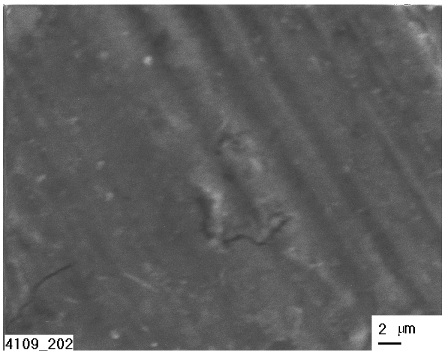

Fig.2. Compacted sample

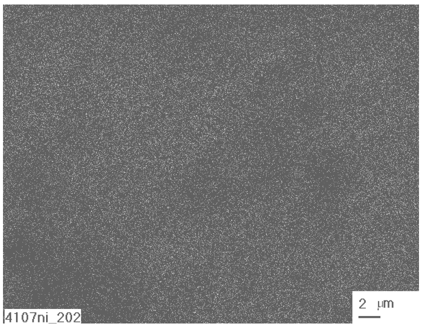

Fig.3. Surface of a compacted sample in NiKα characteristic radiation

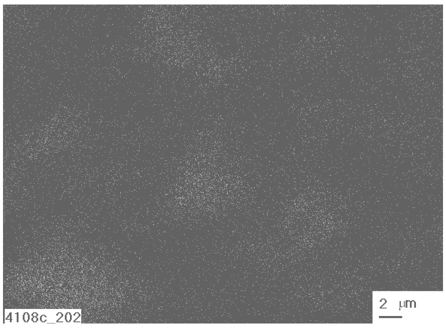

Fig.4. Surface of a compacted sample in CKα characteristic radiation

Hence we have concluded that exo-fullerenes may be produced in non-aqueous electrolytes by the chemical method and the use of metal-organic compounds allows the addition of nickel atoms to a fullerene molecule directly in toluene.