

# THE BIO-NANO-ECRIS PROJECT: A NEW ECR ION SOURCE AT TOYO UNIVERSITY TO PRODUCE ENDOHEDRAL FULLERENES\*

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## Abstract

We are developing a new electron cyclotron resonance ion source (ECRIS) for the synthesis of endohedral fullerenes, which have potential in medical care, biotechnology and nanotechnology. So this ion source is called Bio-Nano ECRIS. It has been reported that ions of fullerenes and carbons-loss fullerenes, such as  $C_{60}^+$ ,  $C_{58}^+$ , ..., are easily produced in ECRISs. Such carbons-loss fullerenes might have an advantage for the production of various endohedral fullerenes. The Bio-Nano ECRIS is designed for the production of endohedral fullerenes. In this paper, the recent progress is briefly summarized; i) Bio-Nano ECRIS project, ii) design aspect of the Bio-Nano ECRIS, iii) results of the initial experiments on the production of the ions of fullerenes and carbons-loss fullerenes.

## BIO-NANO ECRIS PROJECT

### Endohedral fullerenes

Fullerenes have a unique type of inner empty space with their unusual cage-like structures [Fig. 1(a)]. A variety of atoms may reside in this space [1] and form endohedral fullerenes [Fig. 1(b)]. Endohedral fullerenes have novel physical and chemical properties that are very important for their potential applications such as magnetic resonance imaging agents, biological tracing agents, organic ferromagnets and superconductors etc.

Endohedral fullerenes are generally produced by arc discharge and laser vaporization methods [1]. These methods are originally for the synthesis of fullerenes. The soot, which contains fullerenes, is generated by arc discharge or laser vaporization of the pure graphite target. These methods are applied for the synthesis of endohedral fullerenes. By using the encapsulating elements-graphite mixed target in place of the pure graphite target, we can synthesize the endohedral fullerenes. However the atomic species and fullerene species, which can form endohedral fullerenes, are still limited for arc discharge and laser vaporization methods. For example, the production of iron-encapsulated fullerenes has not been successful so far. But it can be applied as magnetic resonance imaging agents. Thus, we aim the production of  $Fe@C_n$  using the

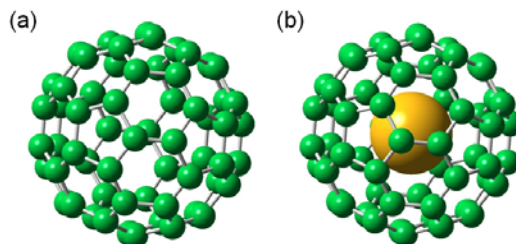


Figure 1: Illustration of (a)  $C_{60}$  molecule and (b) endohedral  $C_{60}$  molecule.

Bio-Nano ECRIS, where @ means that the atoms listed to the left of “@” are encapsulated into  $C_n$ ,  $C_n$  means fullerenes or carbons-loss fullerenes.

Recently the organic chemical synthesis of  $H_2@C_{60}$  has been reported by Komatsu et al. [2]. They demonstrated the synthesis of the open-cage  $C_{60}$ , which has a large orifice (13-membered ring), by an organic chemical reaction. And they synthesized open-cage fullerene incorporating hydrogen. They showed the availability of the open-cage fullerenes, which has a large orifice on their surface, for the production of endohedral fullerenes.

### Fullerenes in ECRIS

Fullerene plasmas and beams have been produced in ion sources, such as electron impact, Nielsen-type, Nier-type, Kaufman-type, radio-frequency and ECR ion sources, for various scientific and practical reasons and purposes [3]. In particular, by using an ECRIS, collision reactions of fullerenes have been studied so far [4]. In an ECR plasma, fullerenes are ionized and fragmented;  $C_{60}^+$ ,  $C_{58}^+$ ,  $C_{56}^+$ , ... are generated. Fullerene fragments (so-called carbons-loss fullerenes) are generated by eliminating  $C_2$  units. We expect that carbons-loss fullerenes might have an orifice (7-membered ring or higher), even though such structure is unstable and transient. Therefore, carbons-loss fullerenes might have an advantage for encapsulating atoms into their inner spheres.

### Our early study

In Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), the encapsulation of gas atoms into fullerenes in ECR plasma has been studied using the ATOMKI-ECRIS, which is designed for the production of multiply charged ions [5]. In 2006, a prototype magnetic structure (the ATOMKI-ECR-B,

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which is equipped with a large plasma chamber and a weak hexapole around it. This ECRIS is specialized for the production of large-sized, low-ionized plasmas and provided the fullerene beams for a number of experiments.) was tested to produce fullerene and iron ions [6]. In 2007, an evaporator using induction heating was tested to produce iron ions, and it demonstrated that this heating method was suitable for operation in the good vacuum [7]. Consequently, a mechanical design for optimum operation to produce endohedral fullerenes in ECR ion source was developed. At present, we have started the investigation of the basic property and the initial experiments of the production of ions of fullerenes or carbons-loss fullerenes by using a mostly completed apparatus. And the manufacturing of an induction heating iron evaporator is in progress.

## DESIGN ASPECT OF THE BIO-NANO ECRIS APPARATUS

### Overview

The Bio-Nano-ECRIS apparatus is designed for the synthesis of the endohedral fullerenes. In other words, this apparatus is specialized to produce the low-charged and large-mass ions and the deposition of the ion beam. The main features of this apparatus are as follows.

- Several evaporation sources (fullerene evaporation and Fe evaporation,...)
- Large plasma chamber to reduce the wall loss of low-charged large-mass ions and to mount several evaporation sources
- Relatively weak magnetic field in order to reduce the synthesis of high-charged ions
- Low extraction voltage and large sector magnet to analyze the ion beam with high mass-to-charge ratio
- Beam deceleration system and substrate holder to do the ion beam deposition

Figure 2 shows the schematic diagram of the Bio-Nano-ECRIS apparatus. This apparatus is composed of four main parts; (1) an ECRIS, (2) an ion beam extraction electrode and focusing lens, (3) a beam analyzing magnet, (4) beam detectors and a deceleration electrode.

The ECRIS (Fig. 3) equips large plasma chamber, two microwave waveguides, fullerene evaporating oven, and gas inlet. The diameter and length of the plasma chamber are 14 cm and 34 cm, respectively. In particular, the diameter of the chamber is larger than that of ECRIS which is for the synthesis of the multiply charged ions. Two microwave sources are an 8 - 10 GHz travelling wave tube (TWT) amplifier and a 2.45 GHz magnetron source. At present, only 8 - 10 GHz microwave is available. 2.45 GHz microwave will be operative in 2009. The fullerene vapor is provided with a resistance heating oven based on the RIKEN micro-oven [8]. The Fe vapor is provided with an induction heating oven. This is now manufacturing. In addition, the optional processing chamber is mountable between the plasma chamber and the extraction electrode. The first tests of these items in the Bio-Nano-ECRIS will be done soon. The magnetic

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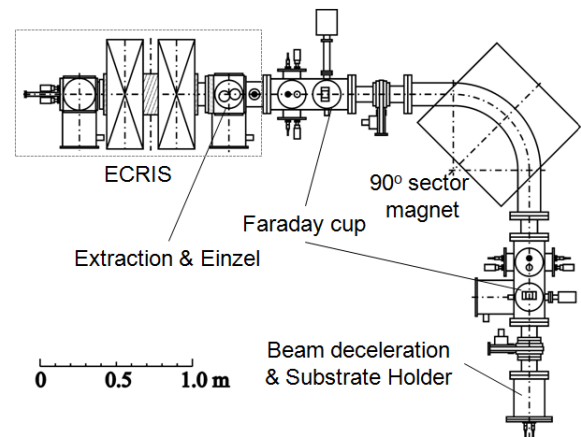


Figure 2: Schematic diagram of the Bio-Nano-ECRIS apparatus.

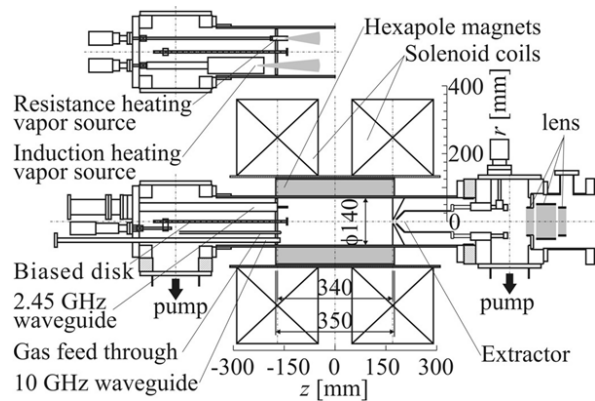


Figure 3: Schematic diagram of the ECRIS.

system for the confinement of the charged particles in the plasma chamber is provided with the mirror coils (axial direction of the chamber) and the hexapole permanent magnet (radial direction of the chamber). The details about the magnetic system are shown in the next section.

Ions generated in the plasma chamber are extracted and focused by electrostatic systems; a movable extraction electrode and an einzel lens. The extraction gap (distance between the plasma aperture and the extraction electrode) is 1 - 6 cm. The extraction voltage is 0.5 - 5 kV. Simulations of the ion beam extraction and focusing are now in progress.

The extracted and focused ion beam is analyzed by a 90° sector magnet according to mass-to-charge ratio. The curvature radius of this magnet is 50 cm. The magnetic field of the sector magnet can be controlled from 0 to 0.8 T. Thus, we can get the mass-to-charge spectrum by sweeping the magnetic field or separate specific ions according to mass-to-charge ratio. This system can transport the 5 kV beams with mass-to-charge ratio of around 800, which corresponds to  $C_{60}^+$  and  $C_{70}^+$ .

The detection of ion beam is done by the faraday cups, which are mounted before and after the sector magnet. At the end of this beam line, a beam deceleration electrode, which can hold a substrate, is mounted. Maximum deceleration voltage is 5 kV.

All these ECRIS and following beam line are evacuated by three turbo molecular pumps (450 l/sec). The pressure in the chamber is monitored by a cold cathode ionization gauge just above each pump.

The specification and normal operating parameters of the Bio-Nano ECRIS apparatus is shown in Table 1.

Table 1: Specification and normal operating parameters of Bio-Nano ECRIS apparatus

Mirror magnets	Solenoid coils
Axial magnetic induction peak (500 A)	0.442 T
Minimum field strength (500 A)	0.165 T
Mirror ratio (500A)	2.68
Hexapole Magnet	Nd-Fe-B
Maximum radial magnetic induction in chamber	0.72 T
Microwave (1)	TWT amplifier
Frequency (1)	8 – 10 GHz
Microwave (2)	Magnetron
Frequency (2)	2.45 GHz
ECR magnetic field for 2.45 GHz	0.0875 T
8 GHz	0.29 T
10 GHz	0.36 T
Plasma chamber diameter	14 cm
Plasma chamber length	34 cm
ECR zone diameter (500 A, 10 GHz)	10 cm
ECR zone length (500A, 10GHz)	23 cm
Fullerene evaporation	Resistance heating oven
Temperature (normal use)	400 – 500 °C
Extraction gap	1 – 6 cm
Extraction voltage	0.5 – 5 kV
Diameter of Extraction electrode	1 cm
Diameter of plasma aperture	1 cm
Analyzing magnet	Solenoid coil, 90° sector, $r = 50$ cm
Magnetic field strength	0 – 0.8 T
Deceleration voltage	0 – 5 kV
Vacuum system	Turbo molecular pump (450 l/sec × 3)

### Magnetic system

As mentioned above, the confinement field of the charged particles is provided with mirror coils and a hexapole permanent magnet. Figure 4 shows the axial magnetic field distribution at the coil current of 500 A. The ECR magnetic field strength for 10 GHz microwave is also shown in the figure. For the coil current of 500 A, the maximum and minimum field strengths are 0.442 T and 0.165 T, respectively. In this case mirror ratio is 2.68. Figure 5 a), b) show the two dimensional contour plot of the hexapole magnetic field (cross-sectional view of the plasma chamber) and the magnetic field distribution along the OA and OB axes.

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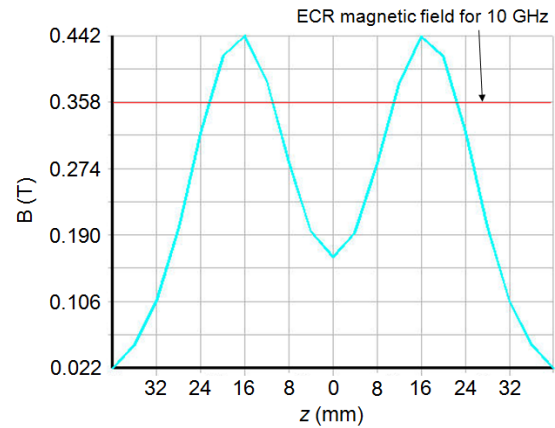


Figure 4: Axial magnetic field distribution at the coil current of 500 A.

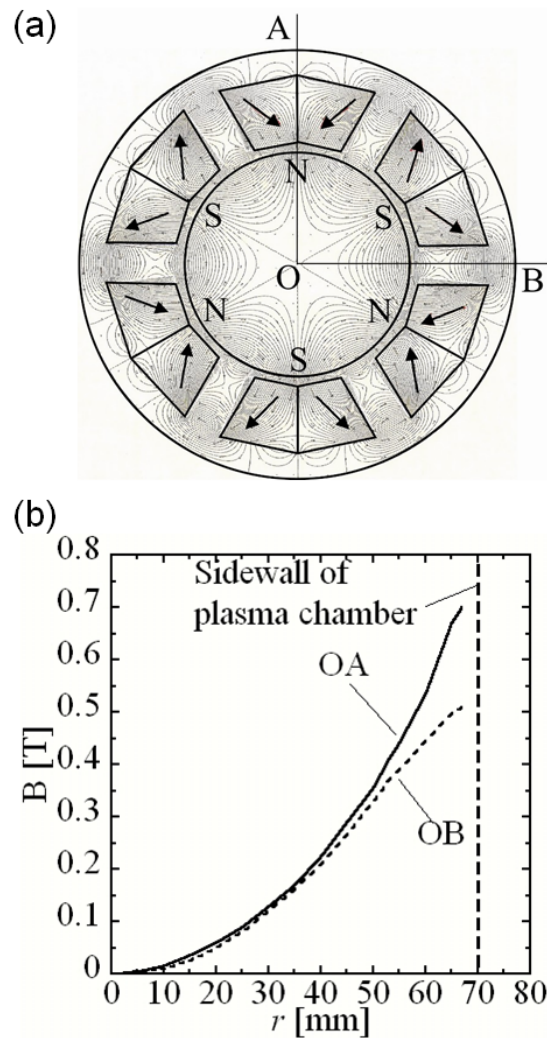


Figure 5: (a) Two dimensional contour plot of the hexapole magnetic field (cross-sectional view of the plasma chamber) and (b) magnetic field distribution along the OA and OB axes.



the OA and OB axes, respectively. Figure 6 is the contour plot of the calculated magnetic field (longitudinal sectional view of the plasma chamber) at the coil current of 500 A. In this case, the ECR magnetic field for 10 GHz microwave is 0.36 T. The corresponding ECR zone for 10 GHz is also shown in the figure. The diameter and the length of the ECR zone at the coil current of 500 A is 10 cm and 23 cm, respectively.

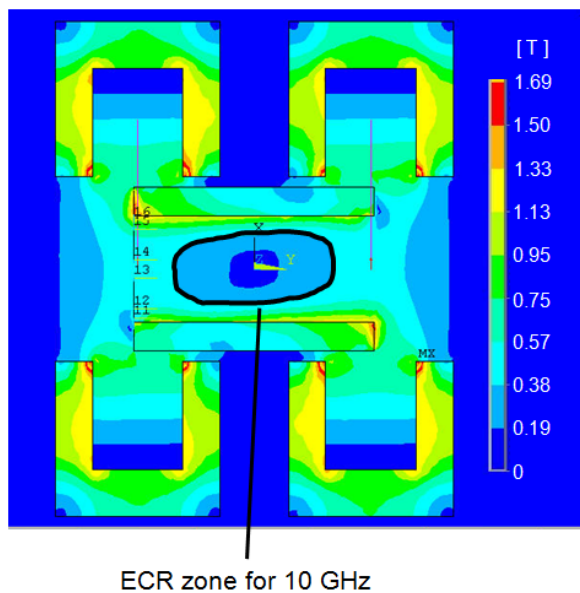


Figure 6: Contour plot of the calculated magnetic field (longitudinal sectional view of the plasma chamber) at the coil current of 500 A.

## RESULTS OF THE INITIAL EXPERIMENTS

### Fullerene ion beam

As an initial experiment of the production of fullerene ion beam, we have generated the pure fullerene plasma and measured the fullerene ion beam spectra. We used pure  $C_{60}$  powder (99.5%, nanom purple, Frontier Carbon Corporation) and pure  $C_{70}$  powder (98 %, nanom orange, Frontier Carbon Corporation) as sources. Figure 7 (a), (b) show the  $C_{60}$  ion beam spectrum and  $C_{70}$  ion beam spectrum, respectively. In case of the  $C_{60}$  ion beam spectrum [Fig. 7 (a)], the measurement conditions are as follows; mirror coil of 500 A, microwave frequency of 9.75 GHz, microwave power of 5 W, extraction voltage of 5 kV, and plasma chamber pressure of  $5 \times 10^{-5}$  Pa. We could generate the  $C_{60}$  plasma without the assist gas (Ar,  $N_2$ , ...). The single-, double- and triple-charged ions of  $C_{60}$  are observed in this figure. In addition, the single- and double-charged ions of carbons-loss  $C_{60}$  are also observed. For the ions with  $m/q$  value less than  $\sim 200$ , it is difficult to analyze because of the complex structure of high-charged fullerene ions and single-charged small carbons-loss fullerenes ( $< C_{20}$ ) ions. The beam intensities of  $C_{60}^+$ ,  $C_{60}^{2+}$  and  $C_{60}^{3+}$  are 400 nA, 800 nA and 170 nA,

respectively. It should be noticed that these values are almost as high as those obtained by using the ATOMKI-ECRIS even though the operating conditions are not optimized.

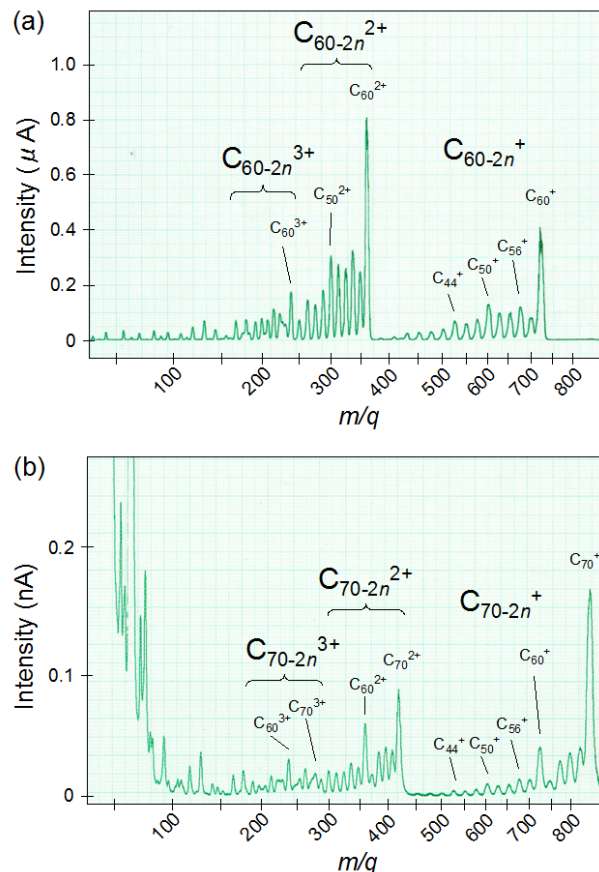


Figure 7: (a)  $C_{60}$  ion beam spectrum and (b)  $C_{70}$  ion beam spectrum.

In case of the  $C_{70}$  ion beam spectrum [Fig. 7 (b)], the measurement conditions are almost same except for the microwave power. The microwave power is 10 W. Basically,  $C_{70}$  ion beam spectrum shows the similar tendency to  $C_{60}$  ion beam spectrum. But the beam intensity for  $C_{70}$  spectrum is much lower than that for  $C_{60}$  spectrum. The reason of this low beam intensity is unclear. We guess that this is due to the lower vapor pressure of  $C_{70}$  than  $C_{60}$ .

For both  $C_{60}$  and  $C_{70}$  ions beam spectra, ion beam currents of  $C_{70}$ ,  $C_{60}$ ,  $C_{56}$ ,  $C_{50}$  and  $C_{44}$  are the (local) maximum in both  $C_{60}$  and  $C_{70}$  ion beam spectra. It is thought that this is because such carbons-loss fullerenes are stable [9]. As mentioned above, we could obtain very clear  $C_{60}$  and  $C_{70}$  ion beam spectrum using a new ECRIS apparatus. We should optimize the operating conditions, such as beam extraction and focusing and examine the beam deposition.

## SUMMARY AND FUTURE PLAN

We have developed the large part of the ECRIS apparatus for the production of endohedral fullerenes. We

have finished the initial experiments of fullerenes ( $C_{60}$  and  $C_{70}$ ) ion beam extraction. We could synthesis the ions of fullerenes and carbons-loss fullerenes and separate them according to the mass-to-charge ratio. In particular, high beam intensity was obtained for  $C_{60}$  ions even though the operating conditions were not optimized. We

think that there is still room for improvement of the beam intensity. In the future, we are planning to do following things; i) optimization of the beam extraction, ii) production of iron ions using induction heating oven, iii) production of iron-encapsulated carbons-loss fullerenes

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