UV Fe I absorption in the carbon-iron arc periphery under formation of carbon-encapsulated iron nanoparticles

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Abstract. The UV (384.5 – 393.1 nm) absorption spectra of Fe I atoms (21 lines) originating from a $^5D_{0,4}$, a $^5F_{1,4}$ and a $^3F_{2,3}$ electronic levels were used to determine the Fe I column density in function of carbon-iron anode composition and the distance from the arc gap, beneath and above the horizontally oriented electrodes. The results revealed a wide variation between the gradients of Fe I column density above and below the arc zone. Also the electronic excitation temperature of the Fe I levels was evaluated.

1. Introduction
The carbon arc route is frequently used for fullerene [1], carbon nanotube [2,3] and carbon-encapsulated magnetic nanoparticles (CE) [4] synthesis. Magnetic CE are promising hybrid nanomaterials with unique potential applications, e.g. in environmental protection [5,6,7]. The systematic studies on the synthesis of CE by carbon arc route have already been performed elsewhere [8]. The ability to control the process of CE growth is of primary importance. The formation of its precursor species, their temporal evolution within the various plasma zones and transport through the specific temperature gradient certainly plays an important role on the diameter, quality and yield of the final product [8]. Because of high temperature, several kK, a variety of carbon species is present: from atoms, ions and simple molecules in the interelectrode gap to the complex carbon clusters at the arc periphery. Obviously, neutral and ionized Fe species, which form the core of CE (e.g Fe@C), as well as atoms of the buffer gas, are also the arc plasma constituents. The detailed diagnostics of the arc plasma was the subject of a previous work [9], in which combined optical emission and absorption spectroscopy was applied to determine the temperature and C$_2$ radical content in function of carbon-iron anode composition. Also, the average density of Fe I atoms in the inter-electrode space was evaluated on the basis of the integrated absorbance of 385.99 nm line.

The aim of this work was to explore the so-called dark zone where the nucleation of iron nanoparticles and coating by graphene layers, thus forming the CEs, takes place, and to find how far iron atom vapor spread out in the reactor volume. To our knowledge such studies have never been carried out. However, some results on the iron content in the arc plasma zone are described elsewhere [9].

2. Experimental
The homogenous anodes used for experiments (0 – 22.5 Fe at. % ) were prepared using a fine graphite powder (1 - 2 μm), blended with Fe powder (6 - 9 μm) and a tar pitch, which was added as a binding
agent. The as-prepared mixtures were then pressed under 2 MPa to form rods of 8 mm in diameter and 30 mm in length. Next, the rods were calcinated under Ar atmosphere at 1000°C for 10 hours.

The experimental system for arc generation and spectroscopic studies is described in detail elsewhere [10]. All experiments were conducted under Ar:H$_2$ (1:1) atmosphere and at constant pressure of 60 kPa. The discharge current was 40 A and the voltage drop varied within the range between 30 and 38 V. The light of a 200 Watt Xe arc lamp was used as a background for absorption spectra, which were recorded with the use of a two-dimensional CCD detector coupled with a spectrograph of 3 m in focal length and 1.6 nm/mm in reciprocal dispersion. The spectral resolution on the CCD detector was 0.0056 nm/pixel. Four dark zones were explored. Locations of the zones are marked by the dashed lines in figure 1. The CCD detector covered about 9 mm of coordinate y and 8.6 nm of the spectral interval.

![Figure 1. Pictorial representation of electrode configuration (side view) and arrangement for absorption measurement. Dashed lines – absorption paths.](image)

The measurements in each zone were associated with the exchange of the electrodes and new positioning of the electrodes against the optical axis of the lamp-spectrograph system.

The absorption measurements were time limited during the discharge, because of generation of a dust. The incident light passing through the reactor undergoes the Mie scattering on the micro-carbon dust particles formed during the discharge. Thus, this effect reduces the reactor transparency. Figure 2 illustrates the time evolution of the reactor transparency in the UV spectral window. The transparency rapidly decreases with the increasing of Fe content in the anode. The reliable absorption spectra could be obtained within a short time interval, about 20 seconds, in case of the highest Fe contents in the anode. Obviously in this case the absorption measurements could be influenced by the largest error.

![Figure 2. Time dependence of reactor transparency](image)
3. General remarks on Fe I absorption

The UV (384.5 – 393.1 nm) absorption spectra of Fe I atoms (21 lines) pertaining to the transition from the $^5\text{D}_{0,4}$, a $^5\text{F}_{1,4}$ and a $^5\text{F}_{2,3}$ electronic levels were used to determine the Fe I column density. The column density (in units cm$^{-2}$) is defined as the product of atom concentration and column length along the line of sight. The examples of the absorption spectra recorded at different positions, below and above the arc discharge are shown in figure 3. The spectrum C contains only lines associated with the absorption from $^5\text{D}_{0,4}$ levels. It should also be noted that as with the distance from the anode the width of absorption lines decreases. It is demonstrated in figure 4, in which the full width at half maximum (FWHM) of some $^5\text{D}_{0,4}$ lines is plotted against the observation coordinate $y$, which is perpendicular to the electrode axis (figure 1). The FWHM follows the population of the levels, hence the most broadened line is that one which originates from the lowest, and thereby the most populated, $^5\text{D}_4$ sublevel. One can assume that the main factor which influences the line broadening is connected with the resonance interaction between atoms of the same kind [11]. Thus the width depends on the local Fe I concentration. Therefore such a line broadening becomes much weaker further from the arc (figure 3, spectrum C). In this zone all the recorded spectral lines are of similar width, which approximately is equal to the width of the apparatus function ($\approx 0.023$ nm).

Figure 3. Examples of Fe I absorption spectra recorded below and above electrodes at $y = -5$ mm (A), $y = 5$ mm (B) and $y = 15$ mm (C). Anode composition: 7.5 at. Fe%.

The Fe I column density was determined taking into account both the FWHM and the value of the absorbance at the line center (peak absorbance). At first, a set of absorption spectra covering all lines under consideration were computed. Three parameters were taken into account, namely Fe I column density, temperature and width of spectral absorption coefficient. The latter one was described by Voigt function ($P_v$):

$$\kappa_\lambda = \kappa_v P_v(\lambda - \lambda_v)$$
The width of Voigt function depends on the damping constant $\alpha$ ($\alpha = \Delta \nu_D/\Delta \nu_L$), i.e. the ratio of Doppler and collision broadening width, which in turn depends on temperature. The as-computed spectra were then convoluted with the apparatus function to be Gaussian with the FWHM equal to 0.023 nm. Next the absorption spectra were transformed into absorbance spectra and a three dimensional data table (three parameters) of peak absorbance of all lines was created. Prior to transformation of the recorded peak absorbance into column density the parameter $\alpha$ was evaluated by comparing the experimental FWHM values with a set of computed FWHM as a function of $\alpha$ and temperature. All the calculations were performed assuming constant temperature and broadening of absorption lines within a column. Three temperature values were considered: 3000, 4000 and 5000 K. Neither the temperature nor the Fe I atom concentration is constant along any column. Therefore the Fe column density output can be converted only to mean concentration.

**Figure 4.** Examples of FWHMs of selected absorption lines vs. coordinate y (see figure 1).

**Figure 5.** Influence of parameter $\alpha$ and Fe I column density on peak absorbance of $^5\text{D}_4$ line (left and right panel, respectively).
The influence of parameter $\alpha$ on the recorded peak absorbance of the $^5D_4$ line for two distinct temperatures and column densities is illustrated in figure 5 (left panel). The example of peak absorbance growth curves for two different temperatures (3000 and 5000 K) and parameters $\alpha$ (5 and 25) are also presented in figure 5 (right panel). Let us note that strong line broadening leads to lowering the peak absorbance and hence to linear dependence of peak absorbance on column density.

Taking into account that the average population of a particular level is proportional to the column density the mean temperature within a column was also evaluated using the Boltzmann plot method. The examples of Boltzmann plots for two distinct column coordinates, 5 and 40 mm, are shown in figure 6. Please note that the points belonging to $^5D_{0,4}$ levels are on a straight line, but with a positive slope coefficient, as it is marked by red lines. Such a graph appearance was characteristic for all absorption spectra regardless the zone and discharge conditions. Therefore to be able to at least evaluate the temperature also in the zones where $^5D_{0,4}$ lines are only present (e.g. figure 3 C) the oscillator strength values had to be modified, i.e. multiplied by appropriate factors.

![Figure 6. Example of Boltzmann plots for temperature determination. Column coordinate y: 5 mm (open markers) and 40 mm (solid markers).](image)

Both, literature and modified oscillator strengths are listed in table 1. One has to highlight here that the plasma inhomogeneity surely had an influence on the adopted oscillator strengths. Therefore the new values require further verification because in terms of accuracy all the literature oscillator strengths are assigned to class A. 

| $\lambda$ [nm] | 386.0 | 388.6 | 392.3 | 385.6 | 387.9 | 390.0 | 393.0 | 389.6 | 390.7 | 392.8 | 392.0 |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| lit.           | 21.4  | 11.9  | 3.2   | 7.3   | 8.8   | 5.8   | 6.4   | 7.0   | 1.9   | 9.9   | 17.7  |
| new            | 8.7   | 6.7   | 4.0   | 5.5   | 6.5   | 5.8   | 5.8   | 8.6   | 4.7   | 9.4   | 23.7  |
4. Results and discussion
The Fe I column density distributions determined in different zones above and below the arc gap are shown in figure 7. The panels A, B, C, and D correspond to different anode composition 1, 7.5, 15 and 22.5 at.%, respectively. The dashed lines indicate the middle of the electrode gap. In each panel the distributions are determined from the set of absorption spectra which were recorded every five seconds after the arc ignition.

From figure 7 it follows that atomic iron distribution in the arc reactor is not symmetrical. Moreover, the Fe species are mostly concentrated above the arc discharge zone. In the space below the electrodes one could detect atomic iron only within the distance less than 10 mm, whilst above the electrodes iron is present even at a distance exceeding 50 mm (e.g. panel A). It is a result of the vertical motion of the carbon-iron vapour caused by convection among other things. As it was mentioned above, the measurements performed for each zone were carried out with new electrodes and their space adjustment with respect to the optical axis. Therefore a very accurate reproduction of measurement conditions was not possible. Additionally, in each experimental run the arc spot randomly attached itself to different places on the anode head surface causing thereby the non-symmetrical erosion of the anode. This all explains the shifts between the sub-distributions seen in figure 7. Nevertheless the overall trend of the atomic iron distributions seems to be correct. One can also conclude that the amount of free iron atoms in the reactor increases with iron content in the anode. It should also be mentioned that in the case of the anode containing 22.5 at.% Fe (figure 7, panel D) the measurements between 40 and 50 mm from the electrodes were not possible because of

![Figure 7. Fe I column density distributions. Content of iron in anode in unit at. %: A – 1, B – 7.5, C – 15 and D – 22.5.](image)
rapid dust formation. Nevertheless, one can expect that the trend in this zone should be similar to those shown in panels B and C.

The results of the mean temperature determination are shown in figure 8. The temperature values at two sides close to the arc show the same decreasing trend, i.e. from about 5000 ±500 K to about 3500 K. The spread of the temperature values in more distant areas is quite significant. Probably this is due to a large fluctuation of dust moving by convection towards the reactor lid. Thus, the dust formed more intensively in the zones located further from the arc plasma may randomly change the local gas temperature. Of course, one cannot ignore the fact that the temperatures in these zones were determined only on the basis of the relative population of a $^5\text{D}(0-4)$ sublevels covering a small energy interval between 0 and 0.12 eV, while the energy of a $^5\text{F}$ and a $^3\text{F}$ levels is about 1 and 1.5 eV, respectively. For the sake of comparison the rotational temperature distributions in the arc discharge zone of C$_2$ radical in both, excited (d $^3\Pi_g$) and non-excited (a $^3\Pi_u$) states are also shown in figure 8. [9]. Obviously, the rotational temperature of C$_2$ in the ground state (a $^3\Pi_u$) can be interpreted as the gas temperature. Therefore one can conclude that close to the arc zone the population of higher iron levels (a $^5\text{F}$ and a $^3\text{F}$) are in non-equilibrium with the gas temperature.

![Figure 8](image)

Figure 8. Mean temperature distributions. Anode composition: 7.5 Fe at. %. Full markers: rotational temperature of C$_2$ in a $^3\Pi_u$(1) and d $^3\Pi_g$(2) states.

![Figure 9](image)

Figure 9. Encapsulation yield and mean diameter of carbon-encapsulated iron nanoparticles vs. anode composition.
Since this work is related to carbon-encapsulated magnetic nanoparticles, some data showing the influence of anode composition on the CEs formation are presented in figure 9 [8]. The data are not shown for 1 at. % Fe, because at this condition the main product consists of single-wall carbon nanotubes [14]. It can be seen that the encapsulation yield gradually increases with Fe content in the anode. The same trend concerns the mean diameter of CEs. These findings are consistent with the above spectroscopic results, especially the data shown in figure 7. The increase of atomic iron density in the gas phase increases the collision rate between iron species and thereby enhances the formation of larger Fe clusters. Consequently it leads to the higher encapsulation yield and larger mean diameter of carbon-encapsulated iron nanoparticles.

5. Conclusions
The diagnostics of the dark zones above and below the carbon-iron arc discharge during synthesis of carbon-encapsulated iron nanoparticles was performed by absorption spectroscopy using UV transitions in Fe atoms. The Fe I column density and temperature distributions were determined. The results revealed different column density gradients. A much higher gradient was found beneath the arc. In this zone the content of atomic iron rapidly decreases and nearly totally disappears ca. 10 mm from the anode edge, while in the upper part of the arc reactor it extends to at least 50 mm. The obtained results clearly indicate that the growth of carbon-encapsulated iron nanoparticles occurs mainly beyond 50 mm from the arc.

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