



# The Origin of the Unusual Electrocatalytical Properties of the Mercury Monolayer Carbon Fiber Electrode - the New Two Dimensional Mercury Phase - a Superconducting/Superfluidic Bose–Einstein Condensate at Room Temperature



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## ABSTRACT

The detailed analysis of the phase transition occurring in the metallic monatomic mercury layer (MMML) deposited electrolytically on the chemically inert carbon fiber is presented.

The electrochemical equivalent (Q) of the MMML, which measures  $\approx 420 \mu\text{C cm}^{-2}$ , denotes that the phase transition results in formation of a new two dimensional mercury phase with a compactly packed perfect quasi-crystallographic lattice.

At fractional coverage of the carbon fiber by the Hg atoms close to the unity at room temperature there are reached the necessary conditions for the Bose–Einstein condensation of the MMML specified by de Broglie wavelength of the order of  $\sim 3.34 \times 10^{-8} \text{ cm}$  and by the weak Hg–Hg and Hg–carbon support interactions.

The compactly packed perfect quasi-crystallographic lattice of the MMML and the high planar density of Hg atoms ( $1.31 \times 10^{15} \text{ cm}^{-2}$ ) creates conditions for the Hg valence ( $6s^2$ ) electrons to form so called the superconducting ‘Cooper pairs’.

The dc biasing, through an entrapped Cu atom connected to the power source, shows that at room temperature the 2D Hg phase possesses superconducting properties confirmed by the transport of the double charged quasi-particles—the quasi electron  $e^* = -2e$  during the positive bias, and the quasi-hole  $h^* = +2e$  during the negative bias.

The superconducting properties at room temperature of the 2D mercury phase are a direct confirmation of the Einstein hypothesis that during BE condensation the added extra bosons collapse to the ground state.

The opening of the superconductor energy gap, compiling 1.26 meV, stipulates a strong absorption by the 2D Hg phase of light in visible domain of the electromagnetic spectrum.

The absorption of *all* incident on the MMML photons confirms that the valence electrons of all Hg atoms in the MMML are ‘Cooper’ paired.

It is shown that the absorbed photon energy is converted to the electrical one in real time through the non-adiabatic Landau–Zener collisional mechanism of energy transfer from the optically excited Hg atoms to the biased Cu atom.

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## 1. Introduction

The low-dimensional systems (LDSs) are of high scientific interest due to the quantization of their electronic states that stipulates exciting novel physical, chemical, optical, electronic properties unreachable for the bulk systems [1].

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Since the mercury monolayer carbon fiber electrode (MMCFE) was developed in 2004 for electroanalytical purposes [2] (successfully realized due to the original procedure of removing (etching) of the surface disordered carbon atoms located preferentially between the graphitic crystallites on the 'skin' layer of the carbon fiber) [3–6]) this low dimensional hybrid nanostructure has shown surprising and unusual electroanalytical properties like picomolar voltammetric sensitivity in the sub second time scale for determination of electrochemically active metal ions  $\text{Pb}^{2+}$  [7], or  $\text{Cu}^{2+}$  [8].

The aim of this work is to reveal the role of the phase transition occurring in the MMCFE at  $\theta_{\text{Hg}} \approx 1$  on the appearance of the unusual electrocatalytic properties on this low dimensional electrode by means of the chronoamperometric measurements of the electrocatalytical active system  $\text{Cu}^{2+/0}$  at microsecond time scale of the experiment during the positive and the negative dc bias of the electrode.

## 2. Experimental

The detailed description of the experimental protocol is presented elsewhere [9]. The data presented here were obtained by application on the working mercury monolayer carbon fiber electrode (prepared by electrolytic deposition of the monatomic mercury layer on the high modulus PAN based carbon fiber VPR-19C (diam. = 7  $\mu\text{m}$ , the geometrical surface area  $0.00159 \text{ cm}^{-2}$ ) of two consecutive chronoamperometric impulses (pulse width  $2\text{--}4 \times 10^{-4} \text{ s}$ ) by jumping the electrode potential from  $-1.2 \text{ V}$  (saturated Ag/AgCl reference electrode) to  $+0.1 \text{ V}$  (the anodic bias) and from  $+0.1 \text{ V}$  to  $-1.2 \text{ V}$  (the cathodic bias). The working electrode was placed into the background electrolyte (0.01 M  $\text{HNO}_3 + 0.01 \text{ M HCl}$  (prepared from AR acids) + 0.01 mM  $\text{SCN}^-$  (prepared from NaSCN (>99.99%, Aldrich)) + 2  $\mu\text{M}$   $\text{Hg}^{2+}$  (prepared by dissolution of high purity metallic mercury (99.9999%) in nitric acid (Aldrich AR))). The overall residual concentration of  $\text{Cu}^{2+}$  was approximately 1.5  $\mu\text{M}$ . The measurements were performed under artificial illumination.

## 3. Results and discussion

### 3.1. Specifying the quasi-crystallographic structure of the MMML

The deposition (or the growth) of the Hg overlayers (or epilayers in terminology of [10]) on solid substrates, either from the liquid [11,12] or from the gaseous phases [13] occur in a special mode, called *layer-by-layer* [14]. This mode implies that the subsequent Hg overlayer starts to grow only after completion of the precedent one that allows in suitable conditions to grow (or to deposit electrolytically) the monatomic Hg layer.

However, this mode does not conduct automatically to the deposition of the perfectly compact monatomic layer because the deposited Hg atoms can accommodate on solid substrate in different forms depending on the substrate crystallographic structure as well on its surface morphology. It is known [15] that on metallic substrates the monatomic Hg layer prefers to adopt the crystal lattice of the substrate due to the van der Waals nature of the bonding between the Hg atom(s) and the substrate.

The PAN based carbon fibers have a quasi-crystalline turbostratic structure where the graphitic (graphene) layers (so called graphitic crystallites) are not oriented strictly in a single X–Y plane [16]. However, during the high temperature treatment the structure of the CF becomes more ordered [17] with a pronounced axial orientation of the crystallites and an increase of their content. The dimensions of the last ones, usually, are characterized by means of the X-ray photoelectron spectroscopy which allows to determine the number of graphitic sheets (the parameter  $L_c$ ) in

such crystallites as well their planar size (the parameters  $L_{a\perp}$  and  $L_{a\parallel}$ ). The last ones in crystallography are depicted as the vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  (plus the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between them in the Cartesian system of coordinates) of the primitive unit cell (PUC) that allows to describe the properties of the crystalline materials specified by their crystallographic structure.

Utilization of original electrochemical procedure of the carbon fiber surface activation procedure let us to obtain reproducible MMML on both the pitch based [2] and the PAN based CF [7,9].

The electrochemical equivalent of the MMML ( $Q_{\text{MMML}}$ ) deposited on the pitch based CF [2] compile  $423 \pm 20 \mu\text{C cm}^{-2}$  whereas deposited on the PAN (polyacrylonitrile) based CF the mean value oscillates around  $420 \mu\text{C cm}^{-2}$  [7],[9]. Regarding the electrolytically deposited Hg atom (with two valence ( $6s^2$ ) electrons) as a solid sphere with the radius  $R_{\text{Hg}}$  (the semi-classical approach), the calculus gives that the PUC of the MMML quasi-crystallographic lattice, satisfying the experimentally measured  $Q_{\text{MMML}}$ , can be presented, at least, in three different configurations (based on the CF properties and the mechanism of the MMML growth), depicted as A, A' and B in Fig. 1. The configurations A and A' contain, respectively, 17 and 18 'extra' Hg atoms (atoms which cannot be arranged by the translational repetition of the simplest rhomb containing 4Hg atoms (A) or a hexagon containing 7Hg atoms (A') (the 7th Hg atom placed inside the hexagon formed by 6Hg atoms) in comparison with the 'normal' PUC with not extra-atoms. The presence of the 'extra' Hg atoms is a compulsory condition for the Bose–Einstein condensation to occur.

The natural metallic Hg is a mixture of 6 stable isotopes [18]  $^{196}\text{Hg}$  (abundance 0.15%),  $^{198}\text{Hg}$  (9.97%),  $^{199}\text{Hg}$  (16.87%),  $^{200}\text{Hg}$  (23.10%),  $^{201}\text{Hg}$  (13.18%),  $^{202}\text{Hg}$  (29.86%),  $^{204}\text{Hg}$  (6.87%). The isotopes with an even mass number are pure bosons (depicted as  $\text{Hg}_b$  in Fig. 1), while those with an odd mass number are composite bosons (depicted in Fig. 1 as  $\text{Hg}_f$ ) due to the fermionic character of the nuclei ( $^{199}\text{Hg}$  (nuclear spin  $I = 1/2$ ),  $^{201}\text{Hg}$  ( $I = 3/2$ )). Consequently, the ratio between the pure bosons and the composite bosons equals  $\approx 7/3$ . Assuming that the PUC contains 81Hg atoms the calculus gives that this ratio is maintained (more or less exactly) if the number of the composite bosons is equal to 19. Thus, the number of 'extra' Hg atoms in PUC (structure A, A') can be associated, roughly, with the number of the non-pure bosons in PUC.

Despite the fact that the configuration B with not extra Hg atoms satisfies the  $Q_{\text{MMML}}$  condition ( $Q_{\text{calc}} = 420.5 \mu\text{C cm}^{-2}$ ) the calculated  $2 \times R_{\text{Hg}}$  in this case compiles 3.39  $\text{\AA}$  that exceeds the distance between two graphitic (graphene) layers equating 3.35  $\text{\AA}$ . One consider that namely this feature of the carbonaceous materials, finely stimulated during the soft electrochemical activation of the CF [7], specifies the electrolytic growth of the compact MMML stipulating the local crystallographic order in the PUC of the MMML with a strong influence on its electronic properties [19].

One consider that the structures A' and A in Fig. 1 are almost equivalent. The only difference, conducting to the apparent two separate structures, lies in the different degree of activation (stimulation) of the carbon atoms on the edge of the graphitic planes, i.e. how close these transversal planes are to the electrode/electrolyte interface (how thick is the 'skin' layer of the CF).

In Fig. 1 is presented also (red marked (online version)) the Cu atom (located in the open nanopore), whose presence within the PUC is of the fundamental importance. Namely its presence allowed us to disclose what, in fact, represents the MMML and how it works in the electrochemical catalysis.

The surface concentration of the Cu atoms is determined by the surface density of the so-called open 'nanopores', the surface defects within the last 1–2 external carbon layer(s), whose width (about 3–

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