Field emission characteristics and analysis of charge flow through graphite based cathodes

1st Mohammad M. Allaham  
Central European Institute of Technology  
Brno University of Technology  
Institute of Scientific Instruments of  
Czech Academy of Sciences  
Brno, Czech Republic  
allaham@vutbr.cz

2nd Daniel Burda  
Department of Physics  
Faculty of Electrical Engineering and Communication  
Institute of Scientific Instruments of  
Czeck Academy of Sciences  
Brno, Czech Republic  
burda@isibrno.cz

3rd Dinara Sobola  
Central European Institute of Technology  
Brno University of Technology  
Department of Physics  
Faculty of Electrical Engineering  
Institute of Scientific Instruments of  
Czech Academy of Sciences  
Brno, Czech Republic  
sobola@isibrno.cz

4th Alexandr Knápek  
Institute of Scientific Instruments of Czech Academy of Sciences  
Brno, Czech Republic  
knapek@isibrno.cz

Abstract—This paper studies the performance of different types of graphite cathodes when operated as field emission electron sources. The tested cathodes were prepared in the form of bulk polymer graphite, bulk pure graphite, and polymer graphite coated with thin layer of insulating material (epoxy resin). The obtained results include X-Ray photoelectron spectroscopy analysis, scanning electron micrographs, the field emission microscope patterns and current-voltage characteristics, and the orthodoxy test analysis results. The importance of this study is summarized in following the pursuit of finding cheap and green electron sources. Moreover, to present a new exotic field emission behavior in the form of emission pulses.

Index Terms—field emission, pulsed field emission, graphite, microflakes, polymer graphite.

I. INTRODUCTION

Field electron emission phenomenon is a special technique in microelectronics. This phenomenon appears when the electric current flows in vacuum gap between two separated electrodes after applying sufficient voltage. The external electric field in the gap reduces the potential energy barrier (PEB) near the surface of the two electrodes allowing electrons to quantum tunnel through at sufficient voltage values. Fig. 1 shows the changes in the shape of the PEB from rectangular to image rounded (IR-PEB) after applying the Schottky image effect, and finally to the reduced image rounded or Schottky-Nordheim potential energy barrier (SN-PEB) after applying an external electric field [1].

In field emission studies, there are two types of cathodes (electron sources): The single tip field emitter (STFE) and the large area field emitters (LAFE), which are synthesized by an array of micro/nano STFEs. In what follows, the model to describe the emission current from LAFE is used since the graphite samples are composed of a large array of microflakes with several pointed nano-tips [2].

The height of the SN-PEB in Fig. 1 is described by the electron motive energy $M_{SN}^z$. After solving the Schrodinger equation for the presented system, the measured emission current ($I$) is described as a function of the applied measured voltage ($V$) and the local work function ($\phi$) of the used material using Forbes extended Murphy-Good equation [3]:

$$I(V) = A_{SN}^1 a \phi^{-1} \zeta^{-2} V^2 \exp \left( -v_F b \phi^{3/2} \zeta \right)$$

(1)

In eq. 1, $A_{SN}^1$ is the formal emission area from a SN-PEB, $\zeta$ is the voltage conversion length that connects between the applied electric field and the measured voltage, $a$ and $b$ are the first and second Fowler-Nordheim constants, and $v_F$ is a special mathematical function known as the shape correction factor [4]. Using eq. 1, Fig. 2 presents the distribution of the measured current as a function of the measured voltage.
and the local work function. In 2019, Richard G. Forbes introduced a modern and more accurate analysis and testing method known as the Murphy-Good analysis plots [1], [4]. This analysis method provides a nearly exact straight line, which provides more accurate extraction procedure for the characterization parameters $A_{SN}$ and $\zeta$. MG-plots have the form $\ln(IV - \kappa) \text{ vs } V^{-1}$ with $\kappa$ as the pre-exponential factor of the MG-plot as can be evaluated if $\phi$ is known using the scaling parameters calculator in [5]. From a MG-plot, $\zeta$ can be obtained from the slope and $A_{SN}$ can be obtained from the vertical axis intercept value [6].

Graphite is an adjacent multilayer of graphene, which is synthesized by parallel planar network of carbon atoms ordered in an uncentered hexagonal structure. The carbon atoms are covalently bounded via the van der Waals forces [7]. Polymer graphite is a mixture of graphite microflakes with a polymer bonding agent, which in general is white clay or (Kaolinite) $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [8].

In this paper, the field emission characteristics from polymer graphite, pure graphite, and coated polymer graphite will be presented. This includes the current-voltage characteristics $I(V)$ and the MG analysis results. Scanning electron micrographs (SEM) are presented to show the difference in structure between polymer and pure graphite samples. Moreover, the SEM results are supported by X-Ray photoelectron spectroscopy (XPS) analysis to prove the purity of the used pure graphite microflakes.

II. METHODOLOGY

A. Materials

1) Pure graphite microflakes cathodes: Graphite microflakes (GMF) are formed by the incomplete combustion (limited supply of Oxygen) of hydrocarbon gases and vapors derived from petroleum sources at temperature of nearly 1400 °C. In this work, the used GMF has the commercial name Vulcan® XC-72 produced by Cabot Inc. The product is mainly high purity 99.99% graphite nanoparticles that can be achieved after ultrasonic treatment of the GMFs.

To prepare the pure graphite cathodes, micro-glass tubes were prepared using the heating-pulling technique. Glass tubes of inner diameter ~1 mm were attached to a holder from one side, and to a pulling drill chuck from the other side. Electrical current is then applied into the heating loop to melt the glass while being pulled down at the same time by the chuck. This process can help to pull the melted glass creating micro-conic tips in the form of micro-glass tubes with inner diameters of approximately 40 µm.

The GMFs were then added inside the glass tube, and ultrasonic treatment was applied to the prepared samples to ensure the GMFs will reach micro-aperture of glass tube. Finally, stainless steel tube of 0.3 mm in diameter was mounted inside the glass tube from the other side to establish the electrical contact between the GMFs and the sample holder (power feedthrough). The results are presented in Fig. 3.

2) Polymer graphite: Polymer graphite cathodes (PGC) can be obtained from the market as micro pencil leads. The combination of polymer and GMFs makes it hard enough to be possible to use. In this paper, authors prepared the required PGCs using the membrane-electrochemical etching technique as described in [2], [9]–[11].

Fig. 4 presents the SEMs of GMF and PGC samples. The structure of GMF is presented in Fig. 4(a and b), where it shows the amorphous structure of pure microflakes. In comparison to the structure of GMF, Fig. 4(c and d) present the structure of PGC, where the existence of the polymer material is clearly visible. In both cases, it is clear that micro-surface of the cathode tip contains large number of random tips act as emission cites, which is a reasonable reason to consider each tip as LAFE.
XPS analysis were obtained using the AXIS SupraTM X-ray photoelectron spectrometer set-up (KRATOS Analytical Ltd., Manchester, UK). The results are presented in Fig.5(a) for the GMF and Fig.5(b) for the PGCs. For the case of GMFs, the results show only tiny amount of oxygen ($\approx 4\%$) and major percentage of pure carbon ($\approx 96\%$). On the other hand, the results for PGCs show higher oxygen percentage ($\approx 13\%$) with additional tiny percentage of Si ($\approx 2.3\%$) and Al ($\approx 1.3\%$), which came from the the Kaolinite.

3) Coated polymer graphite: To prepare the coated PGCs, Elantas PDG Epoxylite® E478 Single-Component Thixotropic Epoxy VPI Resin is used as the coating thin insulation layer. The epoxy is manufactured for high electrical insulation applications with voltages less than 7000 V. The prepared PGCs were slowly dipped inside the epoxy resin to create a thin layer of the epoxy, which will differ in thicknesses due to the random distribution of the microflakes. The coated samples are then baked at 423 K temperature for 6 hours to cure the epoxy layer.

Because of the variation in the thickness of the coating layer from point to point on the cathode tip surface, the ability for electrons to tunnel through the layer will also vary, making it possible for different tunneling phenomena to occur causing different emission mechanisms, which will be discussed later in the following section.

B. Experimental setup

The prepared samples were mounted as cathodes into a traditional and diode configuration field emission microscopes (FEM) [9]. During the experiments, the pressure inside the FEM was held at ultra-high vacuum conditions ($10^{-7}$ Pa). The anode of the system was used as emitted electrons collector and prepared by coating a YAG scintillator with aluminum. The anode was connected to a grounded auto-ranging picoammeter (Keithely 405 autoranging Picoameter) to measure the current-voltage characteristics. Moreover, an autoranging picoammeter branded by Rbd 9103 was also used to record the current-time characteristics at fixed voltage for the case of the coated PGCs.
III. RESULTS AND DISCUSSION

The characteristics of each type of the cathodes were discussed earlier in section II-A of this paper. The results included SEM and XPS analyses for both types of the samples. In this section, the current-voltage \( (I(V)) \) characteristics were obtained and presented for the GMF and PGC cathodes using the FEM. The analysis results were obtained using the MG-analysis plots by considering \( \phi \approx 4.5 \text{ eV} \) as presented in literature for graphite based materials [2]. The FEM results included the field emission patterns that describe the emission current density distribution of the emitted electrons.

For the case of the coated PGC, the current-time \( (I(t)) \) characteristics were obtained and presented instead of the traditional \( I(V) \). This is because the emission process showed a unique behavior as presented later. The applied voltage was fixed at specific voltages where the emission is stable, and the \( I(t) \) were recorded.

A. Current-Voltage characteristics

The obtained \( I(V) \) for the GMF sample is presented in Fig. 6(a) and for the PGC it is presented in Fig. 6(b). The inset of each figure describes the MG-plot analysis plots. For the presented graphs, it is clear that the PGC has more advantageous results since it has much lower threshold voltage (1075 V vs 4000 V) and much higher emission currents at lower voltages \((\approx 900 \text{ nA at 1400 V in comparison to 35 nA at 4800 V})\). To perform the analysis procedure for LAFEs, the macroscopic area \( (A_M) \) for each tip surface were evaluated and it was \( 2.1 \times 10^{-8} \text{ m}^2 \) for the GMF samples, and \( 1.6 \times 10^{-9} \text{ m}^2 \) for the PGC sample. In both cases the macroscopic distance \( (d_M) \) between the two electrodes of the FEM was 1 mm. The analyses results were obtained using the field emission analysis webtool in [5], and the results are presented in Table I. The results include the field enhancement factor \( (\gamma = d_M/\zeta) \) and the formal area efficiency \( (\alpha_f^\text{SN} = A_f^\text{SN}/A_M) \), which are important parameters to characterize the used system in terms of enhancing the electric field near the tip surface and the contribution of the tip surface area in the emission process. From Table I, in the case of PGC, the value of \( \alpha_f^\text{SN} \) lies within a reasonable theoretical range. However, in the case of GMF, the formal emission area has larger values, which indicates that the contribution of electron emission was much higher than the case of PGC. This is also visible from the value of \( \alpha_f^\text{SN} \) for this sample since it has very high value. This result is important to explain the reason behind achieving lower current values at higher voltages for the case of GMF, since the charge density is distributed among a higher surface area, and thus, electron occupation of the energy states were lower and needed higher supply voltages to reduce the SN-PEB. Moreover, \( \gamma \) value for the case of GMF is \( \approx 10 \) times lower than the case of PGC, which means higher supply voltages were needed to provide sufficient field intensities.

B. Current-time characteristics

Following the results presented in section III-A, the PGC were used as base material prepare PGC-epoxy composite cathodes, since PGC provided higher current densities at lower voltages. For this type of hybrid field emission cathodes, the emission process included the appearance of a quasi harmonic pulses of high current densities. For this reason, the supplied voltages were fixed at 1700 V when the emission current had a
 stable value and the $I(t)$ were studied for 1500 s. The obtained results are presented in Fig. 7.

This quasi-harmonic behavior can be explained by considering nano-capacitors that are formed within the coating layer after applying an intense external electric field. The electric field will rearrange the electrical dipoles causing some reorientation process for the direction of the dipoles. As the intensity of the electric field increases, the length of the dipoles will increase which causes to merge the dipoles forming larger dipoles in the form of nano-capacitors. At some point, merging of the formed nano-capacitors will not succeed and instead, a discharge of electrons from the a nano-capacitor to another can occur by a resonate quantum tunneling phenomenon. The latest can occur due to presence of trapped electrons between two potential energy barriers, which can lead to harmonically discharge the electrons from surface of the coating layer to vacuum in the form of intense electron pulses.

IV. CONCLUSION

In this paper, three types of graphite based field emission electron sources (cathodes) were prepared, tested, and analysed. The prepared cathodes were prepared from pure graphite microflakes, polymer graphite, and polymer graphite coated with epoxy resin. The results showed higher advantageous characteristics for the case of the polymer graphite cathodes and for this reason they were used to produce the coated samples. The coated samples showed a unique field emission behavior by emitting intense pulses of electrons with high current densities.

The poor performance of the pure bulk graphite cathodes is related to the limitation of the current flow inside the bulk structure of graphite microflakes. For this reason, as a future work, the project aims to proceed with pure graphite microflakes and study the field emission characteristics from cathodes prepared from shells of pure graphite microflakes, since the shell structure is believed to provide promising field emission characteristics.

ACKNOWLEDGMENT

CzechNanoLab project LM20181110 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements/sample fabrication at CEITEC Nano Research Infrastructure.

Research described in the paper was financially supported by the Internal Grant Agency of Brno University of Technology, grants numbers CEITEC VUT/FEKT-J-23-8307 and FEKT-S-20-6352.

The research was financially supported by the Czech Academy of Sciences (RVO:68081731).

REFERENCES