PREPARATION OF COLD FIELD EMISSION CATHODES WITH ULTRA SHARP TIPS

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Abstract: This article deals with preparation of very sharp cold field emission cathodes made from polycrystalline tungsten wire which is widely used by other researchers and manufacturers. Common manufacturing process of electrochemical etching in NaOH solution is improved by separation of electrolyte surfaces between anode and cathode. This method prevents hydrogen bubbles, formed on cathode, to fine down the electrolyte surface near anode that cause shockwaves which affect the progress of etching. Separation of surfaces leads to sharper tips of the final cathode which is the main goal of my research.

Keywords: electrochemical etching, cold field emission cathode, tungsten, sharp tip

1 INTRODUCTION

Cold field emission cathodes are widely used in electron microscopy where a small and stable source of electrons is required. Cold field emission cathodes differ from thermionic or Schottky cathodes by presence of strong electric field which modifies shape and height of the potential barrier near the cathode surface and allows electrons to secede from the metal surface. Cathodes usually work at high levels of vacuum with relative low potential applied (approximately 200 V) and do not require additional heating like Schottky or thermionic cathodes [1].

Above mentioned cathode can be obatined either from tungsten wire or any other transition metals such as Niobium, Tantalum, Hafnium or Lanthanum. Electrochemical etching is a cathode manufacturing process in which are involved electrolyte (for tugsten usually KOH or NaOH aqueous solution at specified concentration), an anode and a cathode [2]. Tungsten wire acts as an anode and as a negative electrode a chemically resistant stainless steel wire is commonly used [3]. After applying ething potential between cathode and an anode, anode metal is dissolved as cation in the electrolyte and at the same time an equal amount of cation is deposited on the surface of cathode [4]. The rate of dissolution and deposition depends on the applied elecrochemical potential and concentration of the electrolyte solution and also the process of electrochemical reaction is inflouenced by a complex of other electrochemical effects on anode and cathode (e.g. non-uniform concentration of cations in solution, effect of impurities both in electrolyte and on the surfaces of electrodes, local inhomogenities of electric field etc.), but dissolution and deposition are still dominant processes [5]. The main goal of electrochemical etching of cathode is to a obtain sharp metal tip, which a source a stable emission of electron beam with its low fluctuations in an electron microscope system. When the tungsten wire dissolves to an electrolyte, it reaches the point where the bottom part of wire drops off to the solution (from which the name of the method is derived) resulting in rapid voltage drop which is indicated by a steep decrease of current flow through the electrolyte. From this reason, there is a crucial requirement for control system of etching circuit to rapidly disconnect etching potential. If not, the wire tip continues to be etched, leading to decrease of cathode sharpness [6].

Another thing which significantly affects cathode sharpness are hydrogen bubbles formed on the surface of the cathode during etching process. These bubbles are pulled towards the surface of the solution releasing shockwaves when burst which cause deformation of the tip shape and current peaks during etching. To eliminate this effect the prototype for surface isolation between cathode and anode was made and the collected results are discussed in the article.

2 EXPERIMENTAL RESULTS

Electrochemical etching is sensitive method for manufacturing cathodes from metal filament and depends on many aspects. One of these are reactions which occurs on anode and cathode during chemical process. The following formulas describe the behavior of the system:

$$\begin{aligned} W + 8OH^- &\rightarrow WO_4^{2-} + 4H_2O + 6e^- \quad (anode), \\ 6H_2O + 6e^- &\rightarrow 3H_2 + 6OH^- \quad (cathode), \\ W + 2OH^- + 2H_2O &\rightarrow WO_4^{2-} + 3H_2 \quad (system). \end{aligned}$$

The point of interest is the reaction on the cathode where formation of hydrogen gas occurs. As mentioned above, the hydrogen gas cause instability in current flow and also damages the etched filament. In Fig. 1 there is prototype of plastic preparation which separates the surface of electrolyte between anode and cathode thus the hydrogen has not direct impact on anode but the waves may still propagate through the solution.

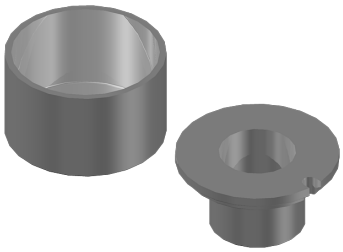


Figure 1: Etching prototype - glass beaker (50 mm x 30 mm) on the left, plastic jig (anode inside, cathode from the outside) on the right. The plastic height is approximately 27 mm which allows the solution to pass through.

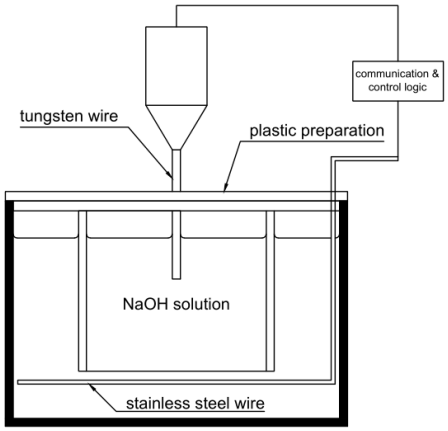


Figure 2: Improved experimental setup with plastic jig included.

The whole setup is shown in Fig. 2 includes glass beaker where plastic jig fits, coiled stainless steel wire with a diameter of 1.2 mm and 2M NaOH aqueous solution. From the previous solution, where the wire with diameter 0.8 mm was used, an additional advantage lies in the higher cathode diameter because of its larger area, where chemical reactions during etching result into formation of hydrogen. This provide smoother etching for the cost of increased rate of ascend of hydrogen bubbles to the surface of the electrolyte.

The Fig. 3, 4 and 5 show cathode tips obtained via improved etching setup in 2M NaOH aqueous solution with different immersion depths and applied potential. All tips are covered with an oxide

layer which was probably formed due to long interval between etching and placing them into electron microscope. However, the best tip radius obtained from improved etching setup was 8 nm which may be considered good enough for further reasearch.

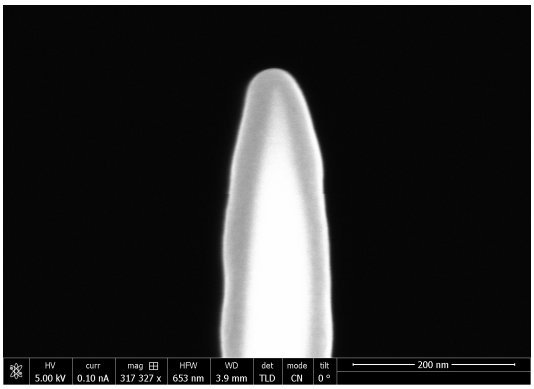


Figure 3: 1. specimen - CN mode (charge neutralization), 70 nm tip, immersion depth 0.8 mm, applied potential 8 V.

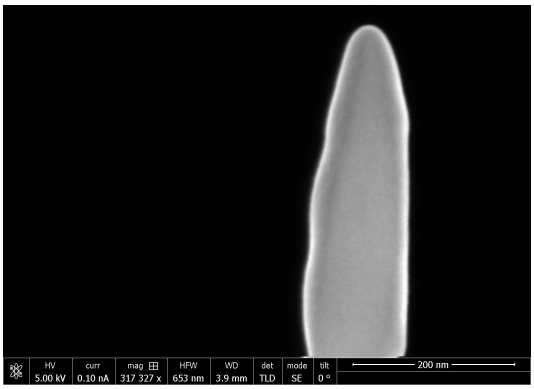


Figure 4: 2. specimen - SE mode (sencondary electrons), 50 nm tip, immersion depth 0.8 mm, applied potential 7 V.

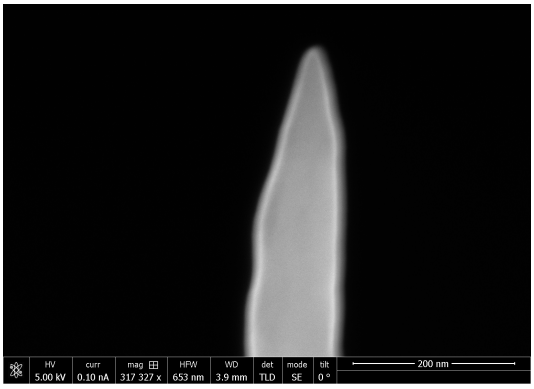


Figure 5: 3. specimen - SE mode, 8 nm tip, immersion depth 1 mm, applied potential 7 V.

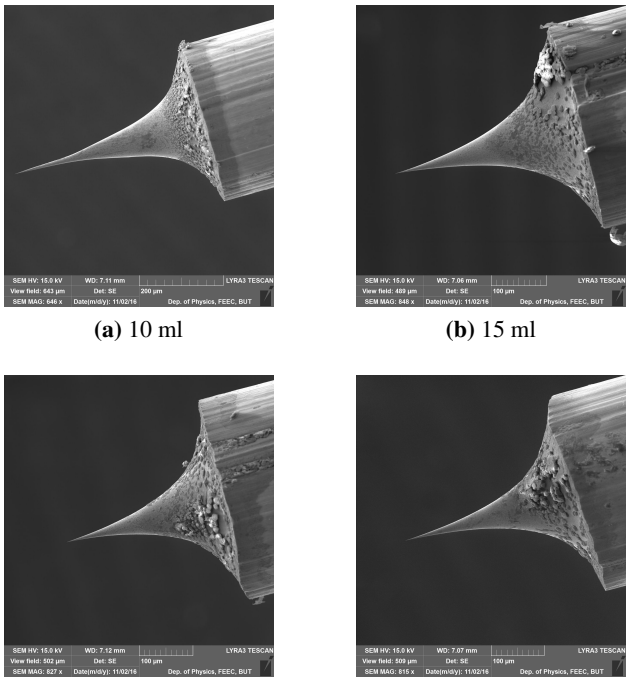
During the tip preparation I have found that the amount of solution cause changes in the length and angle of the cathode tip where the angle is measured between the axis of the cathode tip and pitch.

Specimen No.	**Amount of solution** [ml]	**Tip length** [μm]	**Angle** [°]
1	10	469	3
2	15	348	6
3	20	302	5
4	25	337	4

Table 1: Dependency of the length and angle of the cathode tip on the amount of solution used.

These differences are summarized in Tab. 1. For the low amount of solution the tip length is quiet long which makes it suitable for STM microscopy where the long tip with a small angle is required.

Other studied tips did not show significant differences in properties as shown in Fig. 6. The cathodes were not previously cleaned in demineralized water to prevent possible damage during manipulation.



(a) 10 ml **(b)** 15 ml

(c) 20 ml **(d)** 25 ml

Figure 6: Cathode tips after etching in different amount of solution. The setup is same for each cathode - 2M NaOH electrolyte, 7 V potential and 1 mm immersion.

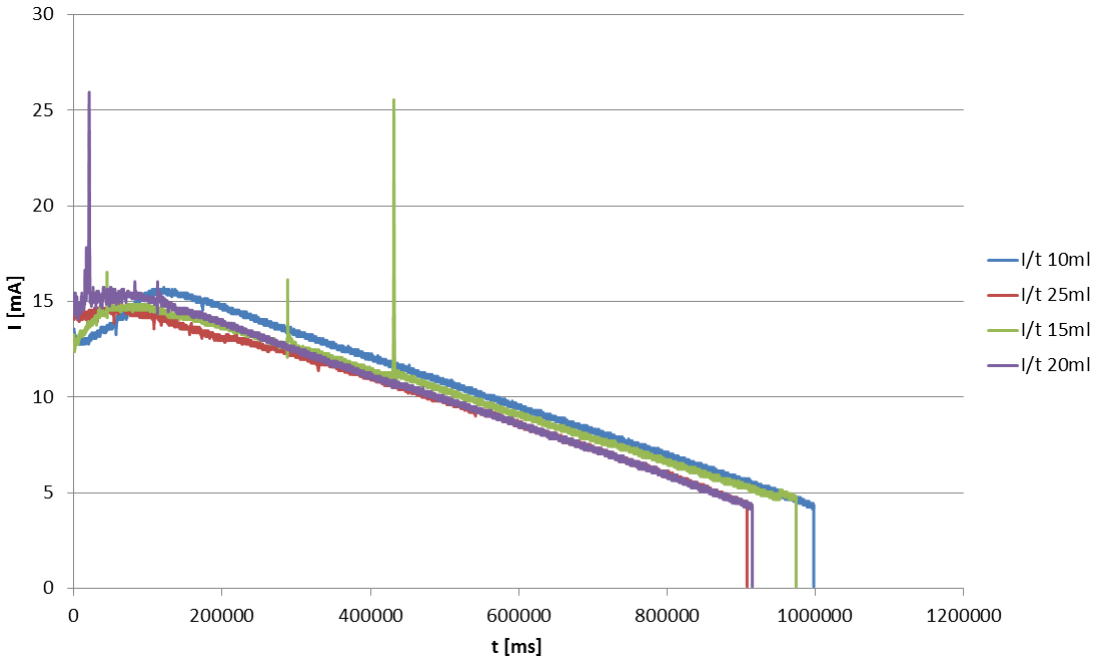


Figure 7: Dependency of etching current of prepared cathodes on process time. Current peaks may be caused by tungsten wire defects or its polycrystalline structure.

Fig. 7 demonstrates dependency of etching current on etching duration for different amount of electrolyte used (10 - 25 ml). With increasing amount of electrolyte the etching time slightly decreases as tip length decreases.

3 CONCLUSION

This article showed the electrochemical etching prototype along with upgraded glass beaker that contains plastic jig for electrolyte surface separation between anode and cathode. Experimental setup brought good results by means of reduction of tips radius to the value about 8 nm, with desirable hyperbolic shape. Using different amounts of solution also showed that the cathode tip length may vary depending on application and the etching duration slightly decreases with a higher volume of electrolyte.

ACKNOWLEDGEMENT

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REFERENCES

[1] L. W. SWANSON and G. A. SCHWIND. Review of ZrO/W Schottky cathode. *Handbook of charged particle optics*. 2nd ed, edited by Jon Orloff. Boca Raton: CRC Press, 2009, xi, 665 p. [cit. 2016-02-20]. ISBN 978-1-4200-4554-3.

[2] M. RICKART and M. BAUER: An improved tip etch procedure for reproducible sharp STM tips. AG Magnetismus, Universität Kaiserslautern, Annual report (1998), p. 53-55[cit. 2016-02-20].

[3] A. I. OLIVA, A. ROMERO G., J. L. PENA, E. ANGUIANO and M. AGUILAR. Electrochemical preparation of tungsten tips for a scanning tunneling microscope. *Review of Scientific Instruments* [online]. 1996, vol. 67, issue 5, p. 1917- [cit. 2015-02-02]. DOI: 10.140631.1146996. Available from URL:<http://scitation.aip.org/content/aip/journal/rsi/67/5/10.14063/1.1146996>.

[4] J. LINDSAY. A pulse/pulse reverse electrolytic approach to electropolishing and through-mask electroetching. Products Finishing. *Gardner Publications Inc.* [online]. HighBeam Research. 2011 [2016-02-20]. Available from URL:<https://www.highbeam.com>.

[5] O. M. BEHR and M. R. BEHR. Environmentally safe Etching. *Chem Tech* [online]. 1991, vol. 21, issue 4, p. 210-215 [cit. 2016-02-20]. Available from URL:<http://www.electroetch.com/chemtech.htm>.

[6] A. J. MELMED, J. The art and science and other aspects of making sharp tips. *Fifth internationl conference on scanning tunneling microscopy/spectroscopy*. 1991, vol. 9, issue 2, p. 601-608 [cit. 2016-02-20].