Electrochemical etching of graphite tips for potential use in nanoscience

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Abstract—The main goal is to find an easy, and more importantly, cheap process of producing sharp tips for the potential use in an atomic force microscope (AFM) or as a source of electrons utilizing cold field emission. This objective is being achieved by the method named electrochemical etching, and the used material is cheap and easily accessible. For this experiment, graphite leads of different hardnesses were used, etched with two types of etching solutions. The first solution contained potassium hydroxide (KOH) dissolved in water and the second contained sodium hydroxide (NaOH), also dissolved in water. Different ratios of chemicals were tried for the manufacturing process. Hardnesses of leads were 2B, B, and HB. After the process of etching, products were examined with a scanning electron microscope (SEM). The radius of tips was measured, and results were compared and evaluated. Stating on the output data of tips, it can be said, that goal was achieved, and tips can be used for their potential purpose. There would be needed another research about how well they fit to work.

Keywords—graphite, electrochemical etching, tips, SEM, conditions

1. INTRODUCTION

The initiation of this experiment is based on searching for cheap materials which can be used as tips for atomic force microscopes (AFM). Usual tips are made from highly expensive metals like tungsten, platinum, iridium, and others. For example, the monthly average price of platinum in February 2022 was 1049$ for the troy ounce (=31,1 grams) [1]. So, this is the reason, why this work looks for an alternative material, which would not be so expensive and yet will satisfy the needs and requirements for this task. In this work, the experimental material was graphite, graphite leads, commonly used for writing/drawing. This material is cheap and very easily accessible on the internet [2] or it can be bought in usual stationery. Another advantage of graphite is electrical conductivity [3], which makes it suitable for the method of electrochemical etching.

1.1. Electrochemical etching

It is a method, where etching is carried out by electricity. Energy is flowing through the circuit, formed by the metal arm (acting as a cathode), etching solution (medium), and graphite lead (acting like anode). Contact of solution and graphite is an area of reaction. The medium used for the process must be an electrolyte because we need electricity to flow through it. As it is generally known, graphite is made from carbon atoms arranged in a hexagonal structure and its charge is positive. So, when the electricity is turned on, carbon atoms want to move towards the cathode, and they are torn off from the structure. The shape of the metal circle secures even consumption of material. This action will manufacture around and sharp tip. When the tip is created and the lower part of the lead falls away, it is essential to stop electricity as soon as possible, because the top of the tip is still in contact with the solution, and electricity is flowing. Subsequent etching would cause harm to the tip quality [4].

2. MATERIALS AND METHODS

2.1. Conditions and data

The idea of researching is to find out the most effective combination of conditions, which will create a perfectly sharp tip. Each hardness met both types of solutions, and all used concentrations of these solutions, at least three times, so it can be checked if the same result was done repeatedly. During all the etching tries, time was measured by the watches. A device used for this work is an etching station for probe production (NT-MDT Spectrum Instruments, Moscow Russia). In total, two types of chemicals, three different concentrations of these chemicals, three types of graphite leads were used. On one pencil lead falls six different conditions, each condition repeated at least three times. Their quality was measured in form of tip radius. The smaller the radius, the sharper the tip. Measuring was implemented with a scanning electron microscope (SEM) Lyra3 (Tescan, Brno, Czech Republic). Settings during measurements were immutable, measuring with a view field of 200μm and accelerating voltage of 10kV.

2.2. Pencil leads

As it was said, commercially accessible graphite leads were used, three hardnesses from the same producer (Pilot, Tokyo, Japan). The marking of hardnesses is HB, B, and 2B. Each hardness depends on the content of clay [5]. Clay is usually additive to graphite leads, more specifically, clay is a term for the mineral named kaolinite. With the content of clay in pencil, hardness can be affected. The relation between hardness and volume of clay is directly proportional. In this case, HB hardness is the same as F-marking, F – stands for the firm and contains the biggest amount of clay, B – stands for black, which has a smaller volume of clay, and 2B has the smallest amount of clay.

2.3. Etching substances

During this research, two different chemical materials were used: potassium hydroxide (KOH) and sodium hydroxide (NaOH). They were used in diverse quantities for dissolving in water. Amounts used for creating multiple solutions were 2g/40ml, 4g/40ml, and 6g/40ml. These chemicals were used because they are quite easily accessible and cheap indeed. They can be bought in the usual drugstore. When they are dissolved in water, chemicals will split into two groups, K or Na and OH group. OH, group is needed and important, because of its negative charge and subsequent carbon attraction.

2.4. Method of tip production

Lead is firmly placed into the holder and goes through the circle of the metal arm. This metal arm is submerged into solution, round space of circular part gets filled by solution and returns to its primary position. Now graphite lead is again in the middle of round space, soaked in electrolyte. Then electricity is turned on and electrochemical etching will start. It will continue until the lead is separated into two parts and the tip loses contact with the solution. At this moment, the circuit is broken, electricity is not flowing anymore, and the process is done.

3. RESULTS

Results are summarized into two tables. **Table 1** represents the results of the KOH solution, and **Table 2** represents the NaOH solution. In the top cell of the column is listed concentration of etching solution. Then each cell underneath represents one hardness with two main information, the arithmetic average of etching time, calculated from all tries in the same conditions, and best-achieved radius from all tries in the same conditions. The format of time in cells is in seconds, and radius sizes are in micrometers (μm).

Table 1: Variations of KOH solution

Concentration of 6g/40ml	Concentration of 4g/40ml	Concentration of 2g/40ml
2B Average etching time: 113s Best achieved radius: 52.07μm	2B Average etching time: 102s Best achieved radius: 27.47 μm	2B Average etching time: 169s Best achieved radius: 11.02 μm
HB Average etching time: 140s Best achieved radius: 15.33μm	HB Average etching time: 381s Best achieved radius: 27.74 μm	HB Average etching time: 442s Best achieved radius: 6.76 μm
B Average etching time: 181s Best achieved radius: 12.81 μm	B Average etching time: 201s Best achieved radius: 10.63 μm	B Average etching time: 317s Best achieved radius: 7.67 μm

Table 2: Variations of NaOH solution

Concentration of 6g/40ml	Concentration of 4g/40ml	Concentration of 2g/40ml
2B Average etching time: 153s	2B Average etching time: 82s	2B Average etching time: 119s
Best achieved radius: 18.47µm	Best achieved radius: 9.6µm	Best achieved radius: 17.3µm
HB Average etching time: 246s	HB Average etching time: 236s	HB Average etching time: 209s
Best achieved radius: 28.04µm	Best achieved radius: 10.47µm	Best achieved radius: 8.69 µm
B Average etching time: 176s	B Average etching time: 91s	B Average etching time: 181s
Best achieved radius: 13.37µm	Best achieved radius: 16.71µm	Best achieved radius: 7.74 µm

Few observations can be described. The first observation is logical, the hardest leads take a longer time for creation than the softest ones. This is happening repeatedly in all cases except one. An interesting case is when hardness B during etching with 6g/40ml KOH solution, has the longest average time of production, although it does not contain the biggest amount of clay. It is not known why this action happens, and there would be needed another research for finding out the reason. This phenomenon is not repeated in different conditions. So, it can be stated that almost in every case, producing time is moving directly proportional to the content of clay.

2.5. Photos of the best tips

These are the photos of the best-produced tips. They were taken by the electron microscope during the examining and measuring process. The yellow inscription is an expression for radius, r stands for radius, and it is measured in micrometers. In the right lower part of the photo is a grey inscription, it is a scale measured in micrometers. Each photo has a title beneath according to conditions of production.

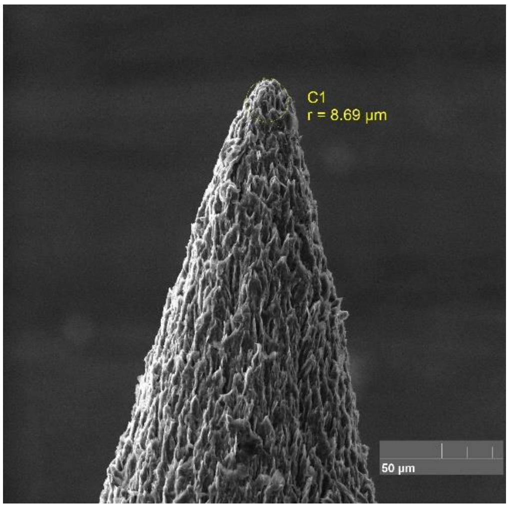

Figure 1:
Concentration of 2g/40ml NaOH, HB hardness

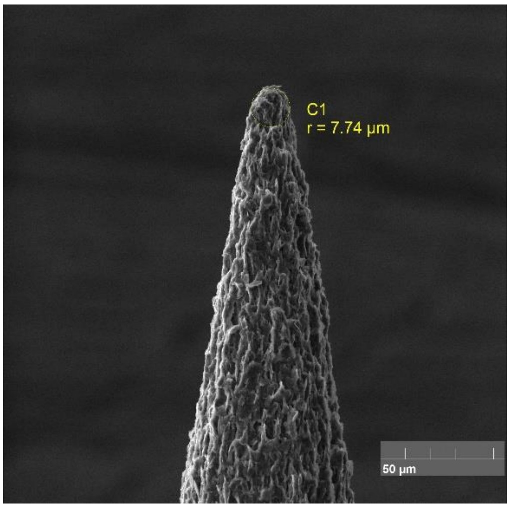

Figure 2:
Concentration of 2g/40ml NaOH, B hardness

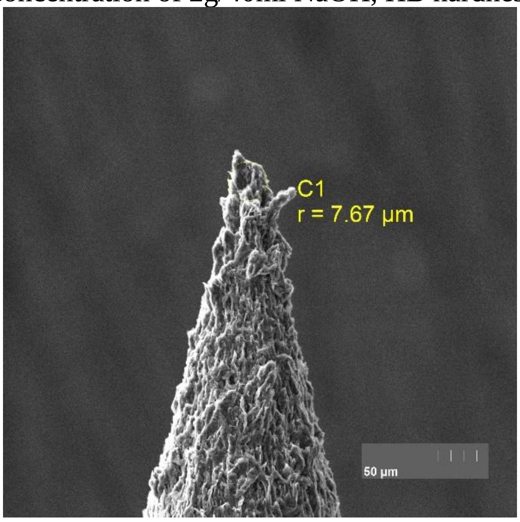

Figure 3:
Concentration of 2g/40ml KOH, B hardness

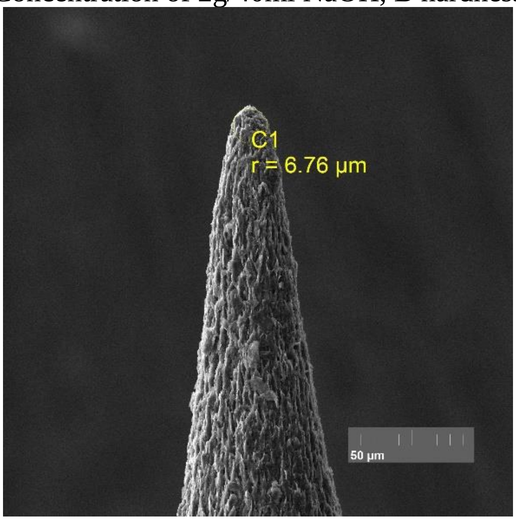

Figure 4:
Concentration of 2g/40ml KOH, HB hardness

4. CONCLUSION

After monitoring the results, several statements can be made. The best results were achieved with the weakest solutions and the worst with the strongest solutions. It cannot be stated that each hardness acts the same in equal conditions. Three times repeated conditions of 6g/40ml KOH and hardness HB, gave very different radiuses (1. 58.39µm, 2. 15.33µm, 3. 34.65µm). From this example is clear, that equal conditions which can be set, do not guarantee the same result. This phenomenon occurs with other conditions too. What can be stated is, that the average radius of tips decreases with the concentration of the solution. The average radius in 6g/40ml KOH is 26.73µm, in 4g/40ml KOH 21.94µm, and in 2g/40ml average radius is only 8.43µm. The same decreasing process happens with the second type of chemical. The best tip was produced with conditions of 2g/40ml KOH and with the strongest hardness HB. On the contrary, the worst tip was produced with the strongest concentration of 6g/40ml KOH and with the softest hardness 2B. In total, it can be stated that this method of producing is capable of creating tips almost sharp enough to be used in SEM or AFM. Almost sharp means that some additional sharpening must be done. For example, with a focused ion beam (FIB) but this process could be another research in the future. The life expectancy of this type of tip is certainly lower than usual metal tips because graphite is a much softer material than tungsten or platinum. But the time and price of manufacturing are a lot lower, so it is profitable to choose this method and save both, time and money. Even if this research is realized on small scale with limited options, quite interesting and good-looking results are created. It is important to invest in this type of research in the future because it opens new possibilities for cheap tips fabrication and usability.

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