VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS
MECHANIKOS FAKULTETAS
POLIGRAFINIŲ MAŠINŲ KATEDRA

Gabrielė Keraitė

DIDELIO LAIDUMO ELEKTRODŲ ANGLIES PAGRINDU SPAUSDINTIEMS SUPER KONDENSATORIAMS TYRIMAS

RESEARCH OF HIGH CONDUCTIVE CARBON BASED ELECTRODES FOR PRINTED SUPER-CAPACITORS

Baigiamasis magistro darbas

Spaudos inžinerijos studijų programa, valstybinis kodas 621H74001
Gamybos inžinerijos studijų kryptis

Vilnius, 2017

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POLIGRAFINIŲ MAŠINŲ KATEDRA

TVIRTINU
Katedros vedėjas
(Parašas)
doc. dr. Nikolaj Šešok
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Vadovas	doc. dr. Eugenijus Jurkonis (Moksl. laipsnis/pedag. vardas, vardas, pavardė)	(Parašas)	2017.05.29 (Data)
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BAIGIAMOJO DARBO UŽDUOTIS:

Bandymų keliu ištirti technines galimybes spausdinti šilkografiniu ir/ar giliaspaudės būdais aukšto laidumo anglies pagrindu superkondensatorius. Tam:

- analizuoti dažų (mikstūrų) elektrodams paruošimą ir modifikacijas;
- elektrodinių (bei elektrolitinių) sluoksnių spausdinimas;
- paruoštų dažų (mikstūrų) ir spausdintų sluoksnių svarbių parametrų charakterizavimas (klampumas, paviršiaus šiurkštumas, sluoksnio storis, elektrinis laidumas);
- atspausdintų superkondesatorių su sukurtais elektrodiniais sluoksniais charaterizavimas bei elektrinių parametrų (elektrinės talpos) įvertinimas.

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MSc. Thomas Weißbach, Chemnitz University of Technology, Print and Media Technology Institute

Vadovas .... *doc. dr. Eugenijus Jurkonis*
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(Parašas)

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Annotation

Currently used conventional manufacturing processes for electronic components such as supercapacitors (capacitors) production are expensive and can not ensure necessary market demand of fast chargeable power sources. This leads to research and development of more affordable and less expensive production methods. Therefore, in this thesis shown successfully created, fully printed and functional supercapacitor made by employing screen and stencil printing technologies from cheap and easily available materials (paper, carbon, phosphoric acid).

In the thesis are given characteristics of created and tested ink mixtures with carbon particles for electrodes; characterized important ink parameters such as rheology and sheet resistance as well as layer thickness, surface roughness and electrical performance of printed layers. Presented investigation description shows main steps how functional supercapacitors construction was created. Described how most efficient materials and their combinations were selected with the help of important parameters measurements.

Presented first steps of possible printing manufacturing concept for supercapacitors production by employing industrial printing systems.

Keywords: Printed electronics, supercapacitor, EDLC (Electric double layer capacitor), screen printing, stencil printing, paper, CNT (Carbon nanotubes).

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Pavadinimas **Didelio laidumo elektrodų anglies pagrindu spausdintiems super kondensatoriams tyrimas**
Autorius **Gabrielė Keraitė**
Vadovas **Eugenijus Jurkonis**

Kalba: anglų

Anotacija

Šiuo metu naudojami tradiciniai elektronikos komponentų tokių kaip superkondesotorių (kondesatorių) gamybos būdai yra brangūs, neužtikrintų reikiamo rinkos poreikio greit įkraunamų energijos šaltinių panaudojimo atveju. Tai motyvuoja ieškoti naujų, pigesnių gamybos alternatyvų. Baigiamajame darbe, parodyta, kad panaudojant šilkografijos ir trafaretinės spaudos technologijas, lengvai prieinamas ir nebrangias medžiagas (popierių, anglį, fosforo rūgštį) buvo sėkmingai sukurtas, atspausdintas ir išbandytas funkcionuojantis superkondesatorius.

Darbe pateikiama elektrodų gamybai sukurtų ir išbandytų įvairių dažų mikstūrų, turinčių anglies dalelių, charakteristikos; charakterizuoti svarbūs dažų darbiniai parametrai, tokie kaip - klampumas, elektrinė varža, o taip pat ir spausdintų sluoksnių storis, paviršiaus šiurkštumas, elektrinis laidumas, varža. Pateiktas tyrimo aprašymas parodo pagrindinius žingsnius sukuriant veikiančio superkondensatoriaus konstrukciją. Parodyta kaip parametrų matavimų pagalba atrenkamos sėkmingiausios kondensatoriaus gamyboje naudojamų medžiagų kombinacijos.

Pateikti galimi pirminiai spaudos būdu sukurtų superkondensatorių pigios masinės gamybos koncepcijos žingsniai, naudojant pramonines sistemas.

Prasminiai žodžiai: Spausdinta elektronika, superkondesatorius, “EDLC” (elektrinis dvigubo sluoknio kondesatorius), šilkografinė spauda, trafaretinė spauda, popierius, “CNT” (anglies nanovamzdeliai).

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Parenkant ir įvertinant medžiagą bei rengiant baigiamąjį darbą, mane konsultavo mokslininkai ir specialistai: , MSc. Thomas Weißbach, Chemnitz University of Technology, Print and Media Technology Institute. Mano darbo vadovas doc. dr. Eugenijus Jurkonis.

Kitų asmenų indėlio į parengtą baigiamąjį darbą nėra. Jokių įstatymų nenumatytų piniginių sumų už šį darbą niekam nesu mokėjęs (-usi).

(Parašas)

Gabrielė Keraitė
(Vardas ir pavardė)

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I. INTRODUCTION

Motivation

Today printing industry is facing two major issues. One, industry can not sell as much as it can produce, another one, that more and more information has been provided in digital form. This situation increasingly promotes worries and encourages look for other markets to motivate growth of printing industry, not a destruction. Since the world digitization rapidly grows it would be smart for printing companies to take a little bit more active interests and actions into another markets such as printed electronics [1]!

Printed electronics in abstract terms is a combination of various technologies and materials, which provides cost –effective, flexible, extremely thin and light -weight electronic devices. One of major advantages of this new field technology is that, it allows produce electronic devices in high volume with comparably low cost. This new technology field, which adapts conventional printing methods to manufacture electronics is still young and rapidly growing, there are still plenty of things to learn and study. However, there are niches where advantages of printed electronics are already undeniable. Most promising areas of application are smart packaging, RFID (radio-frequency identification) tags, OLEDs (organic light -emitting diodes), printed batteries, solar cells, capacitors and many others [2].

Research objectives

Currently used conventional technologies to produce standard silicon based supercapacitors and other electronic components (or entire electronical devices) are expensive. That is why there is urgent need to produce affordable electronics using effective but low-cost materials and manufacturing technologies. Therefore, the main goal of this thesis was to extend the knowledge of carbon based printable electrode materials and with a combination of other inexpensive materials (carbon, paper, phosphoric acid, PVA) produce low cost but high conductive fully printed supercapacitors. The idea was to find the best combination of materials that works best with used printing methods (screen/stencil printing) and gives great performance in the final device. Second objective was to pave the way of this concept for the development and adjustment to the massive production employing gravure roll -to -roll printing technique.

Developed inexpensive mass production of low cost functional devices could solve cost- related problems and open doors for printers into new markets. Paper based printed supercapacitors could be integrated and/or could replace lot of currently used bulky traditional capacitors in many applications like automobiles, trucks, trains, airplanes, and etc. While (printed) supercapacitors are comparably new electronic elements, there is still a lot of space for materials, fabrication technique, construction and other important factors development.

II. PRINTED ELECTRONICS INDUSTRY INSIGHTS

In this chapter, there is short overview of printed electronics market forecasting 2014-2025 with reference to “Market research report”. According the reference report, printed electronics is analyzed by distributing it into smaller segments such as materials, technology, device and region [3].

The global market of printed electronics was evaluated with 3,02 billion USD in 2015 and is expected to grow significantly due to printed electronics is gaining a great acceleration with its integration into electronics industry [3].

According the “Market research report”, the material market segment, which includes conductive inks – one of the most important printed electronics components as well as substrates will be major and most probably largest income generating segment during the whole forecast period in printed electronics field [3].

Based on technologies, the printed electronics market is divided into screen, inkjet, gravure and flexographic printing technologies. Where Screen printing technology gave the highest income in 2015 (Fig. 1) and also is expected to lead the field over the prognosis period [3].

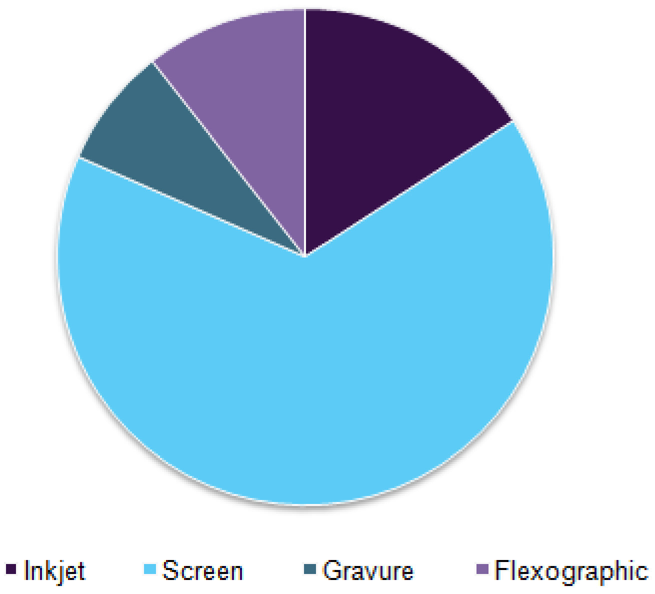

Figure 1 Global printed electronics market by technology, 2015 [3]

Based on devices, the printed electronics market involves radio frequency identification (RFID), photovoltaic, display, lighting and many other devices. Printed electronics technology is experiencing stable adoption rate in sensors, medical, printed batteries and media devices section. In 2015, the largest market shares were occupied by display devices and photovoltaic devices and also are expected to dominate during forecast years [3].

Overviewing the regional insights, the leading regional market of printed electronics in terms of income in 2015 was Asia Pacific. The significant growth is expected in the consumer products applications [3].

Printed electronics is also anticipated to grow in Europe and North America as a result of increased investments in Research and development as well as increasing printed electronics technology adoption in many different industrial applications like RFID, lighting and photovoltaic devices [3].

III. PRINTING AS ADDITIVE MANUFACTURING TECHNOLOGIES FOR ELECTRONICS

Screen printing

Screen printing sometimes named as silk screen printing or serigraphy is a low cost printing technology mostly used for décors on textiles, glass, dishes and advertising paper prints. Nowadays, it is used in various industrial manufacturing processes. Recently it's employment increased significantly in electronics industry due to technological simplicity and flexibility. Screen printing allows to produce thin and thick layers [4].

Screen printing process consist of two main parts flood stroke and print stroke shown in Fig. 2 Firstly the screen has to be fixed above the substrate leaving a certain small gap between. Then ink is loaded onto the screen and the coating blade spreads ink onto the screen filling the openings of the screen without touching the substrate. Then goes print stroke where squeegee transfers the ink onto substrate by pressing it through the open areas of the mesh [4].

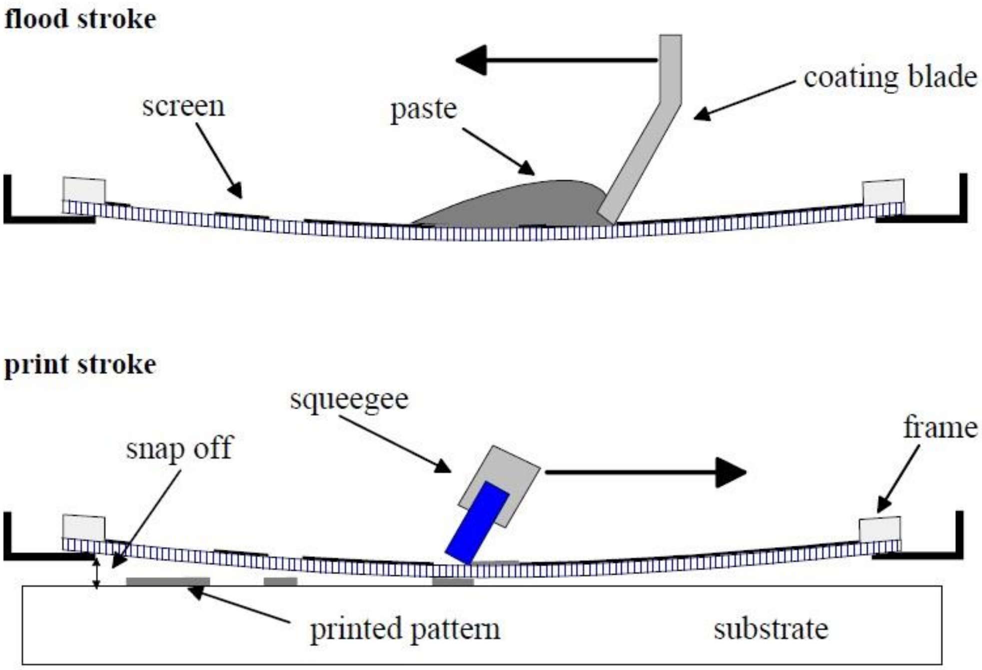

Figure 2 Scheme of screen printing process [3]

Screen printing inks are high viscous, average printing viscosity is 1.5 -2.0 Pa s but can be much higher, it also has tendency to bubble when printing [5]. To achieve high quality print out factors as printing process (squeegee pressure, printing speed, etc.), ink composition (viscosity, rheology, solids etc.) substrate (surface tension, surface roughness, etc.) printing equipment (positioning capability, parameter controls, etc.)) squeegee (hardness, shape of edge, etc.) screen (mesh count, mesh opening, etc.) [6].

Inkjet printing

Inkjet printing is another widely used printing technology for printed electronics. It is a process when ink is sprayed from nozzles onto substrate without any carrier. It is classified according drop generation continuity into two main mechanisms: continuous inkjet, drop on demand inkjet. In the continuous inkjet process ink flow is continuous but only some part of it (which are small drops of ink) is deposited onto substrate. In drop of demand inkjet printing only required amount of ink drops, are generated and deposited onto substrate. Continuous inkjet printing is also divided according deflection process into binary and multi-deflection. In binary deflection process drop can be in one of two states: charged which means that drop is deposited onto substrate or uncharged when drop is deflected into electrical field and goes back to ink reservoir. In multi-deflection process drops are charged with different charges which deflects them into different directions onto different spots on substrate when they are passing through the electrical field [7] Fig. 3.

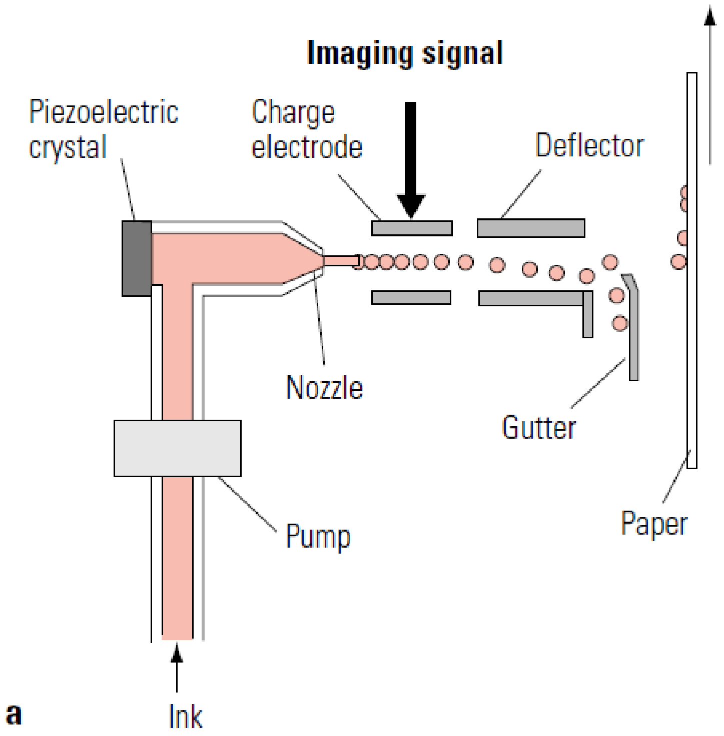

Figure 3 Functional principle scheme of continuous (binary) inkjet printing [6]

Drop on demand can be divided into few variants by drop generation technology. The thermal inkjet process where ink drop received by heating ink until it starts to evaporate where the vapor bubble ejects ink drop due to its exerted pressure (Fig. 4 (b)). In piezo inkjet due to change of ink chamber shape which is cause because of piezoelectric effect, the drop is formulated and ejected from the nozzle (Fig. 4 (c)) [7].

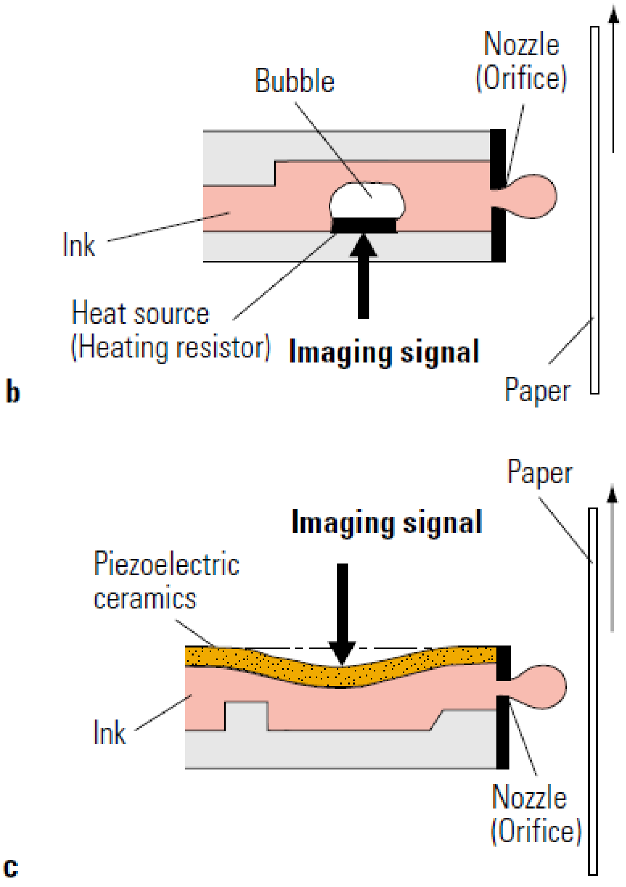

Figure 4 Functional principle schemes of drop on demand (b) thermal inkjet system, (c) piezo inkjet system [6]

This technology allows very accurate positioning, is non –contact, additive technology which ensures less consumption of used materials. Technology works with very small bet very accurate ink volume and its deposition on certain defined areas, which allows a high precision with micrometric resolution. Furthermore, it has low demands for inks and substrates. All these features allows to employ this technology in production of printed electrodes [8], transistors [9], and light emitting diodes [10].

Despite it’s advantages technology also has some cons: slow process, reliability and sensitivity for particles for instance, high concentration inks or dispersions which has particles might clog the nozzle.

Gravure printing

It is a very simple and of one of the easiest printing technologies to work with. The printing process (Fig. 5) is based on, gravure cylinder (which is engraved or etched and has a certain pattern), ink bath, doctor blade and impression roller. As it was already mentioned the printing cylinder has a specific engraved pattern which has cavities called cells. These cells are filled with the ink when printing cylinder is rolled into ink bath. The excess quantity of the ink is scraped off the cylinder by a doctor blade before the ink is transferred onto the substrate. The transfer of the ink onto substrate is direct from engraved cells [11].

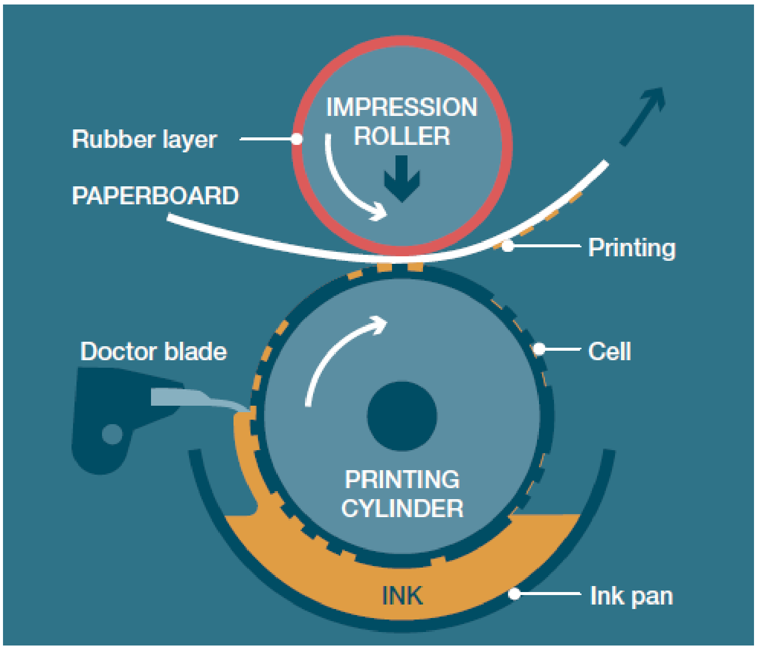

Figure 5 Gravure printing process scheme [10]

This printing technology works with low viscosity inks [11]. Gravure printing is one of the most promising roll -to -roll methods for the mass printed electronics production. It can produce a significant amount of production and could be cost –effective. Gravure printing allows to print very thin films. The thickness of printed films with rotogravure depends on the area and depth of the engraved cells, on the structure of the ink, as well as on the printing cylinder and line speed. All in all gravure printing is a lot promising technology for near future as massive production method for printed electronics.

IV. ELECTRICAL ENERGY STORAGE DEVICES

Nowadays most popular and probably best-known electrical energy storage device is a battery. To be more precise rechargeable batteries, which are used in very many applications [12]. Most common and well- known application for rechargeable batteries are in smartphones, portable computers, notebooks and etc. Beside batteries, there are also other energy storage devices, like capacitors or supercapacitors often found used in memory back-up systems, industrial power and energy management as well as in consumer electronics [13] and many other applications. Currently a certain type of batteries are able to store significantly large amount of energy but they are very bulky and also needs comparably long time to be charged and discharged. Capacitors are much more quickly chargeable and dischargeble but they can store much less energy than batteries. Supercapacitor (sometimes known as ultracapacitors) is device, which is "placed" in between batteries and capacitors and is able to hold much more energy than conventional capacitor and be charged/discharged in a very short time.

Fig. 6 shows different electrical energy storage devices power and energy densities. Where batteries shows low power densities but high energy densities and that is why they usually are used in applications which needs longer term energy storage. Supercapacitors show lower energy densities comparing with batteries but much higher energy densities. There is also a huge difference in charge/discharge time where supercapacitors need only around 1s to proceed and batteries take few hours.

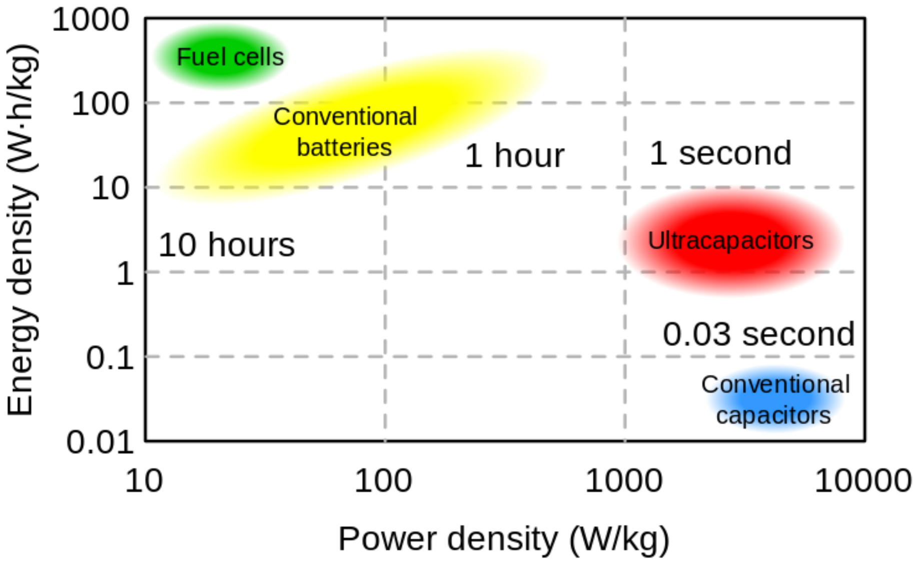

Figure 6 Power and energy densities of different electrical storage devices [13]

V. CAPACITORS

Today there are variety of various kinds of capacitors which often are classified according the cell design, charge storage mechanism, device configuration, and many others factors, but more accurate classification is according used dielectric and its physical state where three main groups are defined. Which are: electrochemical, electrolytic, nonelectrolytic (Fig. 7). Supercapacitors also called electric double layer capacitors (EDLC) can be further specified according material combinations. Recently there is a huge need and interest of energy storage devices which could provide a good energy and power densities, would be reliable and could serve for a long time [14].

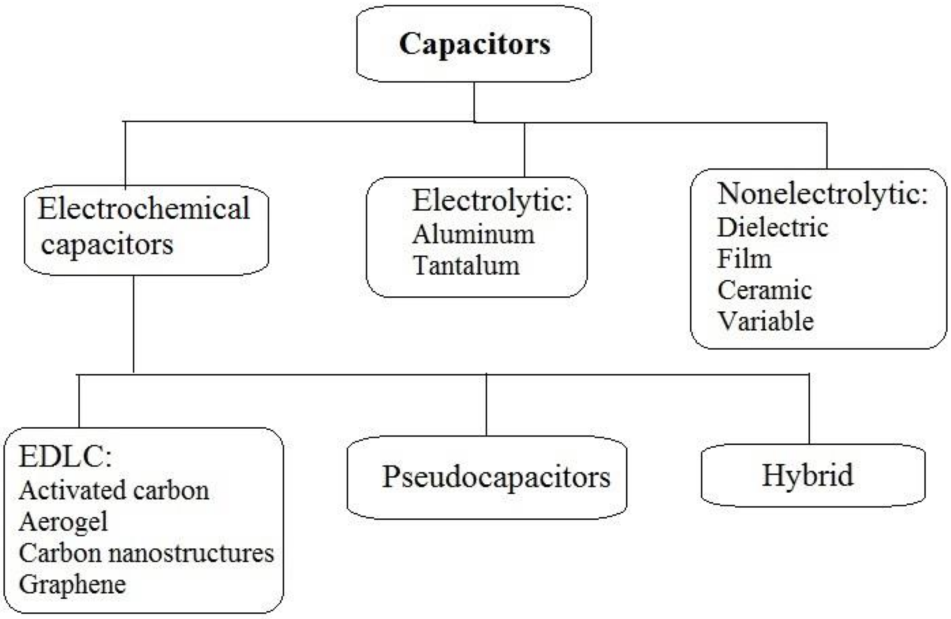

Figure 7 Capacitors calssification. Inspired by [14]

Conventional capacitors principle

Conventional capacitor consists of two plates (electrodes) and dielectric medium (air). To charge the capacitor voltage is applied to the electrodes, which forces positive and negative particles to move toward the surface of electrodes of opposite polarity. After capacitor is charged and connected to a circuit it will behave exactly reversible which means it will be a voltage source for some time till it becomes discharged. The capacitance of capacitor is defined as C is measured in farads (F) and described as charge Q on each electrode divided by voltage V between them [14]

(1) $C = \frac{Q}{V}$

A typical conventional two plate capacitors capacitance C is proportional to the area A of each electrode and the permittivity of dielectric ε and inversely proportional to the distance D between the electrodes.

(2) $C = \frac{\varepsilon_0 \varepsilon_r A}{D}$

Where ε_0 is the permittivity of free space, ε_r dielectric constant.

Therefore, three main criteria have main influence for the capacitors capacitance which are:

- Plate area (electrodes area)
- Distance between the plates (electrodes)
- Dielectric properties

Electrochemical capacitors (ECs)

ECs are often called with variety of different names, which are often associated with company's name or a brand where they were manufactured. Such names are ultracapacitors, supercapacitors, double-layer capacitors, power capacitors and etc. However since the market of ECs is growing there is more and more need for one united name and most likely tendency is for supercapacitors name [14].

Electric double layer capacitors

ELDCs is formed from two electrodes which are separated with a separator which prevents electrodes from electrical contact and all the space between the electrodes is filled with electrolyte. When charging the ELDC capacitor the two oppositely charged layers are at the interface between the electrolyte and electrode (Fig. 8). There are a lot of various models which describes double layer mechanism invented by different scientists. One of the most meaningful models was the Helmholtz double layer model (where he stated that two oppositely charged layers are formed at an electrode-electrolyte interface and are separated by atomic distance) and others such as Gouy Chapman, Stern [14].

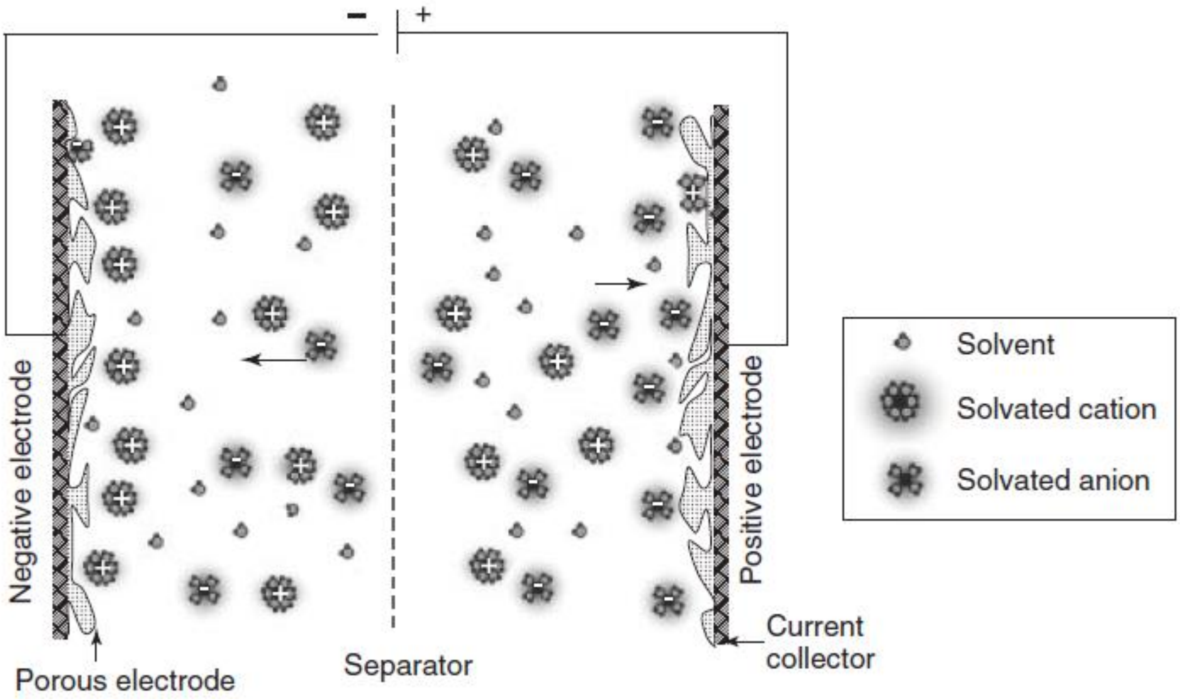

Figure 8 Schematic representation of EDLC based on porous electrodes [14]

In general, ELDC does not differ a lot from a conventional capacitor it stores energy using same charge separation. The most significant difference is that ELDC can store much higher capacitance, which is obtained by porous materials, which are characterized as high surface area materials.

Pseudocapacitive electrochemical capacitors

Capacitors, which stores energy not electrostatically but due to electrochemical reactions, are called pseudocapacitors. Pseudocapacinate is when some materials are available to utilize fast and reversible reactions at their surface. The energy storage is happening due to reversible redox reactions of electroactive materials [14].

Hybrid electrochemical capacitors

Hybrid electrochemical capacitors are also known as asymmetric supercapacitors. There are lot of different hybrid capacitor systems possibilities by coupling redox-active materials. As it written in the *Supercapacitors* book „This approach can overcome the energy density limitation of the conventional EDLC because it employs a hybrid system of battery-like (faradic) and capacitor-like (non-faradic) electrodes, producing higher working voltage, and capacitance. With these systems, one can certainly achieve twice or triple enhancements in energy density compared to the conventional EDLC“ [14].

Supercapacitors applications

Today, a lot of applications and technologies are in great need of energy storage systems that has ability to store and deliver large amounts of energy very quickly, that is why they are suitable to replace electrochemical batteries in variety of applications. For example in solar power applications, medical industry like longer -lasting cardiac pacemakers [15] and many other devices and applications. A huge interest of supercapacitors is growing in automotive industry. To be more precise into applications like hybrid electric vehicles. Recently manufactured new hybrid vehicles usually turns off the engine when vehicle fully stops, to turn it on again the vehicle uses large amount of energy, which is stored in supercapacitor. ”Maxwell Technologies offers a line of supercapacitor-based modules that range up to 3000 F. It has sold over 600,000 supercapacitors for this start-stop application in hybrids” [16]. Few other automotive applications recently were commercialized. Which are hybrid-electric transit buses in China and United states [17], electric braking systems in passenger cars [18]. Supercapacitors also used as memory protection into computers, consumer electronics and communication applications as well as for security alarm systems, uninterruptible power supply systems and other applications [16].

VI. PRINTABLE CARBON BASED SUPERCAPACITORS

In this thesis, printed supercapacitors were produced on the basis, of electric double-layer capacitors. The goal was to use paper as a very cheap and affordable substrate (also extremely light and thin) as well as carbon materials for active layers and phosphoric acid with PVA polymer for electrolyte. The main idea was to print it (every layer) with flat screen printing method.

Carbon types used for electrodes

There is a great variety of different carbon types, which can be and are used as electrode materials for EDLC capacitors. Carbon -based materials are very often used materials as electrodes due to it's low-cost, variation of form (sheets, fibers, powders, tubes and etc.), porosity also because it provides large surface area.

1. Activated carbon

Activated carbon nowadays is most widely used electrode materials because it has large surface are and is comparably cheap material and has relatively good electrical properties. Usually active carbon is produced from carbonaceous materials like coal, wood or fruit shells using thermal or/and chemical activation processes. Activated carbon can achieve very high surface areas depending on activation methods and original materials used to develop activated carbon [13]. Surface area of activated carbon can be high as 3000 m^2 g^{-1} [14].

2. Activated carbon Fabrics

Activated carbon fabrics can be directly used as active materials for electrodes and they do not need any additional binders. Activated carbon fabrics usually are developed from polymeric fibers like rayon and polyacrylonitrile. After activation, they also have comparing large surface area, which varies from 1000 to 2000 m^2 g^{-1}. Though, the cost is not that low of these precursor material to obtain activated carbon fabrics, which limits their usage only for very specific EDLC applications [14].

However, Activated carbon has been commercially used as one of main electrode materials for supercapacitors its application is still limited to a certain markets because of its limitation in energy storage. Despite it can produce a high surface area, its pore size and distribution also as pore structure are still challenging [13].

3. Carbon nanotubes (CNT)

CNT are made of carbon atoms linked in hexagonal shapes and rolled up in a “chicken wire” structure. Carbon nanotubes have extraordinary mechanical, thermal and electric properties due to their specific pore structure. Recently, they have attracted scientist attention as materials for supercapacitors electrodes. There are two main characterized groups of carbon nanotubes: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT), both have been investigated as materials for electrodes. In Fig. 9 shown SWCNT and MWCNT. CNT have compared high electrical conductivity as well as spectacular strength and stiffness, which refers to a good support for active materials and to high power electrodes. However, their surface area can be very variable from 50 to 1315 m^2 g [19].

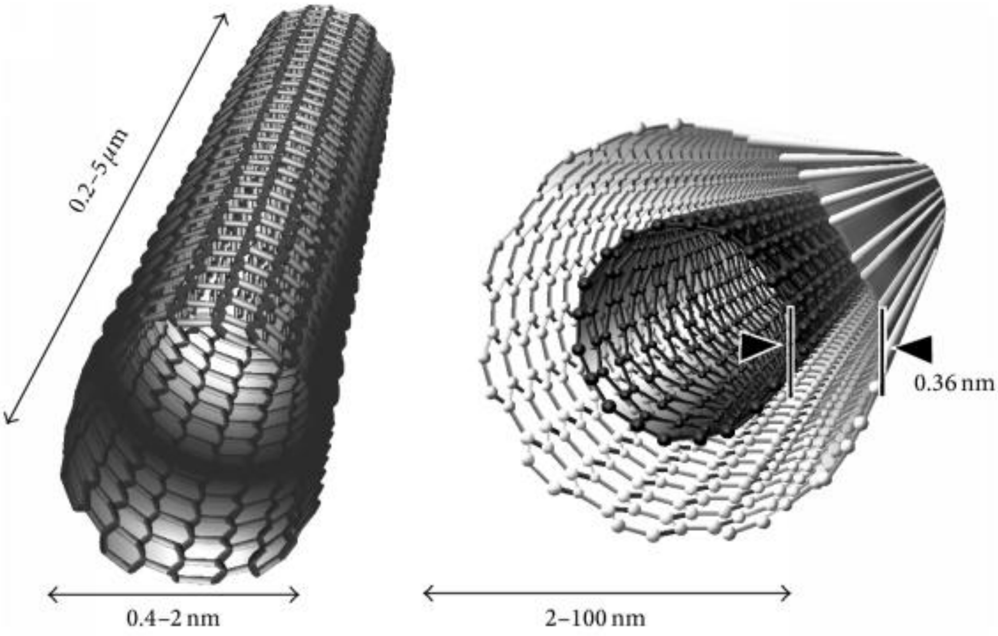

Figure 9 Carbon nanotubes: on the left SWCNT on the right MWCNT [20]

4. Other carbon materials

Carbon aerogels and carbon onions, also are known as suitable materials for supercapacitors. Mainly, there are two most important factors, which has a big influence of supercapacitors electrode materials selection. Those are high surface area and good electrical conductivity.

Carbon aerogel is described with the following characteristics. It is ultralight, has possibility to be used without additional binders and is highly porous material. However, despite it has a high surface area (from 592 to 2371 m^2 g^{-1}) due to high internal resistance, the electrical charge storage capacity is relatively small [13].

Electrolytes

The final performance of supercapacitors depends on two main factors: selection of electrode material which can define the capacitance of supercapacitor and used electrolyte, which determines the operational voltage [14].

There are three main groups according which electrolytes for EDLC are classified:

- Aqueous
- Salts dissolved in organic solvents
- Ionic liquids

Aqueous electrolytes have comparably the lowest operating voltage which is somewhere ~1 V when organic electrolytes have 2,5-2,7 V, ionic liquids 3-6 V. Furthermore, aqueous electrolytes have low cost and high experimental conductivity at 20℃, when organic electrolytes has low and ionic liquids very low experimental conductivity at 20℃ and high cost [14].

VII. MATERIALS AND EXPERIMENTS

This chapter describes the preparation of materials used for supercapacitors and manufacturing steps and methods to produce printed supercapacitors.

Materials

Initial experiments were made with seven different substrates (two conductive materials and the rest absolute isolators) used as primary base materials to print on necessary layers to build a printed supercapacitor. Used substrates with some specifications and manufacturers given in Table 1.

Table 1 Substrates as basis material for supercapacitors

Substrate	**Manufacturer**	**Grams per square meter g/m^2**	**Thickness, µm**	**Other parameters**
Aluminum foil	Ess Dee Aluminium Ltd., Mumbai, India	-	76	-
Zinc coated paper	Unknown	-	175	-
Polyethylene terephthalate MELINEX® 453 2 mil (50 microns)	DuPont Teijin Films Chester, USA	-	50	-
Filter paper	GRÜNPERGA Papier GmbH, Grünhainichen, Germany	80	129	Uncreped
Crystal Standard w/s A528662 (G1)	GRÜNPERGA Papier GmbH, Grünhainichen, Germany	30	21	Pergamin bleached, water-safe
Crystal Standard A529287 (G2)	GRÜNPERGA Papier GmbH, Grünhainichen, Germany	30	21	Pergamin bleached
Super Clear A530275 (G3)	GRÜNPERGA Papier GmbH, Grünhainichen, Germany	32	21	Pergamin bleached

Five inks from four different manufacturers were tested on this research. Ink details given in Table 2.

Table 2 Conductive commercial inks

Ink	**Manufacturer**
AQUACYL 0301 Carbon nanotubes/water mixture (AQ0301)	Nanocyl SA., Sambreville Belgium
AQUACYL 0501 Carbon nanotubes/water mixture (AQ0501)	Nanocyl SA., Sambreville Belgium
Conductive compounds C-200 Carbon resistive Ink (CC)	Applied Ink Solutions, Hudson USA
EMS Cl-2001 (EMS)	Engineered Materials Systems, Inc. Delaware, USA
Du Pont 7105 Carbon conductive composition (DP)	Du pont, Delaware, USA

For the active layer (electrode) development it was used AQ 0301 with some solvents and additives in different ratios. Used solvents and additives for active layer development were:

- BYK-023 defoamer provided by BYK-Chemie GmbH, Wesel Germany
- BYK -361N provided by BYK-Chemie GmbH, Wesel Germany
- 2-propanol provide by Sigma-Aldrich. Co. LLC
- 1-methoxy-2-propanol provide by Sigma-Aldrich. Co. LLC
- Distilled water (18,2 MΩxcm) made with water purification equimpnet TKA GenPure, Wasseraufbereitungssysteme GmbH, Stockland Germany
- 85 % H_3PO_4 provider unknown.
- Polyvinyl alcohol (PVA) provided by Merck KGaA, Darmstadt Germany

For electrolyte layer development there were made 2 mixtures of 85 % H_3PO_4 and PVA (10 % wt) (DI water) solution in different ratios 1:1 and 1:2.

Experiments

All samples were printed with semi-automatic screen and stencil printing equipment EKRA SL-X1 produced by EKRA Screen Printing Technologies (part of ASYS Group). Different screen printing meshes provided by Sefar AG, Heiden Switzerland were tested:

- PET 1500 120/34 YPW
- PET 1500 90-40 YPW
- PET 1500 48-70 WPW
- PET 1500 61/64 YWP

Two different printing technology methods screen printing and stencil printing were used to print and test inks as well as other mixtures for certain layers of the supercapacitor. Various printing speed was used to have understanding if it has any effect in the printout. All printing was made in the room temperature. Tested printing speed:

- 200 mm/s
- 150 mm/s
- 100 mm/s
- 50 mm/s
- 20 mm/s

1. Preparation (printing) of current collector layers

The current collector layers were prepared using screen printing method with printing screen mesh PET 1500 60-64, printing machine EKRA X1- SL (Fig. 10). Printing was made on all substrates mentioned before. Commercial CC ink was used as a current collector layer. Samples were printed using 150 mm/s speed and dried in the oven at 80 °C temperature for 5-7 min.

Figure 10 Semi-Automatic Screen and Stencil Printer EKRA X1- SL

2. Contacts preparation for non-conductive substrates

Contacts were necessary for used paper substrates due to its non-conductivity. Contacts in a form of lines (Fig. 11) were printed on prepared samples with collector layer with printing machine EKRA X1-SL printing speed 150 mm/s screen mesh PET 1500 100-40, silver ink Du Pont 5028 with 10% DBE (Dibasic Ester) and dried at 130 ° C for 10 min.

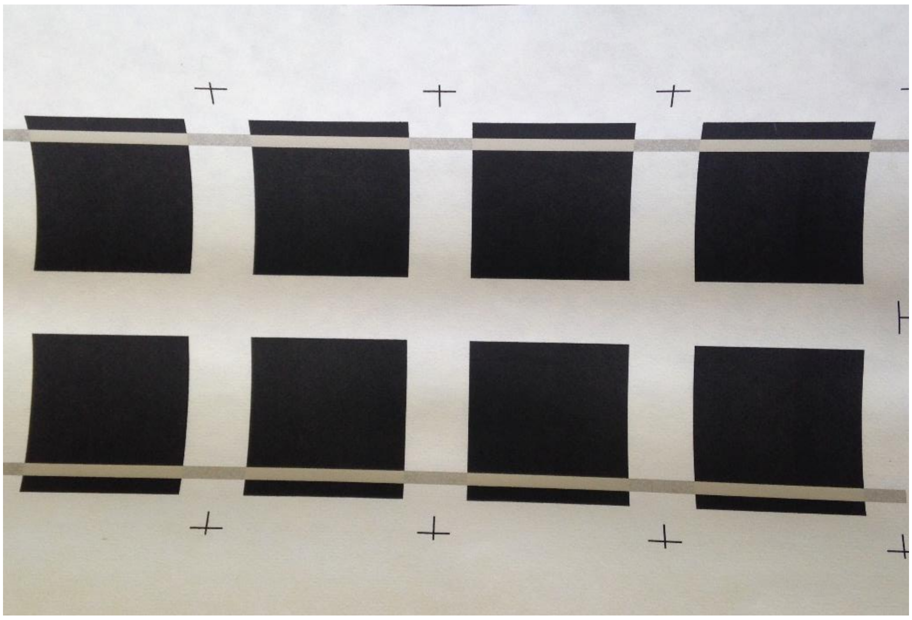

Figure 11 Prepared filter paper cells with current collector layer and silver contacts

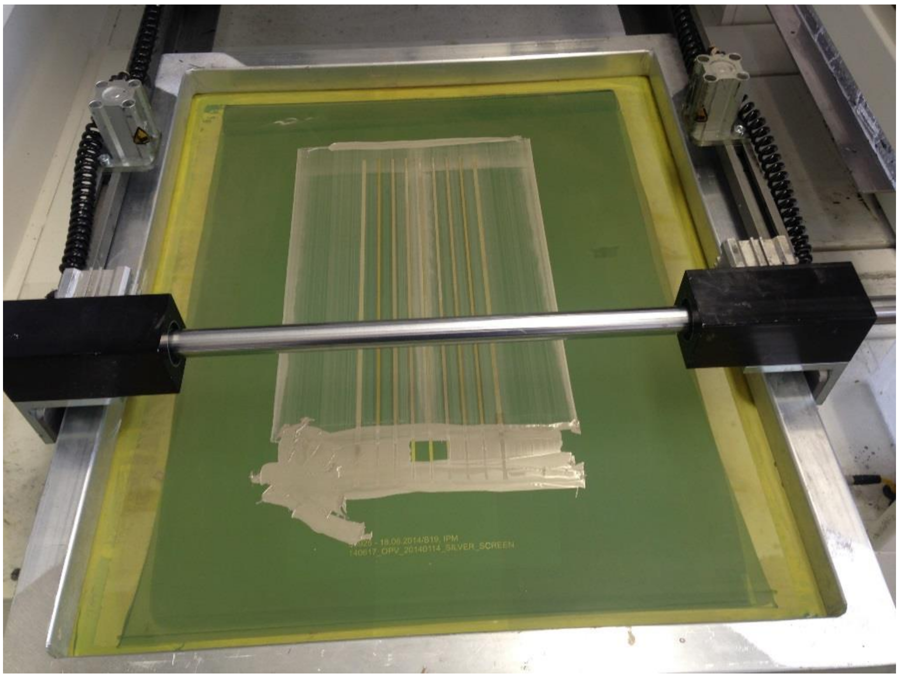

Figure 12 Conctacts printing process

3. Preparation of active layer (electrode) materials

Main ingredients were AQ 0301, PVA (10% wt) solution, H3PO4 (85%), Distilled water and some additives (additional solvents, antifoaming agents). It was tried to make some different mixtures with same ingredients but with different concentration ratios. A certain amount of H3PO4 (85%), PVA (10%) solution, AQ 0301, distilled water, 1-methoxy-2 propanol were added in an empty vial. The amount of added material was measured weighting it with electronic balance Presica Series XB 220A. When all ingredients were added the mixture was stirred for few minutes by hand, then sonicated for 15-18 minutes with a probe sonicator SONOPULS HD 2070, BANDELIN electronic GmbH & Co. KG. The sonication used to ensure that agglomerates were disrupted and CNT were distributed. In total 15 mixtures with different concentrations were made (Fig. 13). All mixtures were made under same conditions following same above described steps.

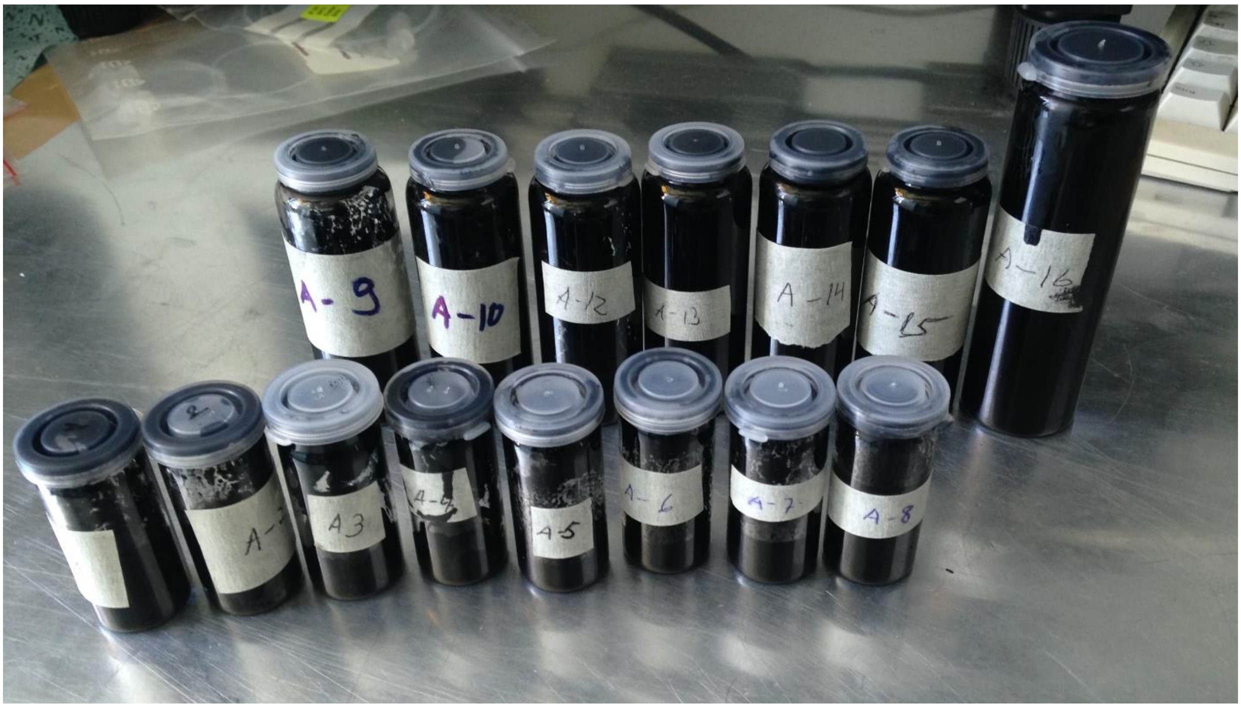

Figure 13 Prepared mixtures for active (electrode) layer testing

4. Active layers (electrodes) preparation (printing)

Electrodes were prepared by printing prepared mixtures on prepared samples with current collector (and contacts only paper substrates) layer. Printing was carried out with printing machine EKRA SL-X1 screen printing method with a screen mesh PET 1500 48-70 and stencil printing method. Samples were left to dry in a room temperature (~25°C) for 30-40 min.

5. Electrolyte material preparation

The material for electrolyte was made from 10 % PVA solution and H_3PO_4 (85%). Both ingredients were mixed together with ratios 1:1 and 1:2 preparing two mixtures. The amount of each material added in a mixture was weighted with electronic balance Presica Series XB 220A. Mixture were stirred by hand for few minutes and then left for 2 hours on roller mixers (CAT) and then taken away and left to rest in peace for 8-10 hours in order to make air bubbles disappear before applying it on samples.

6. Electrolyte layer preparation (printing)

Electrolyte layer was printed on prepared samples with the current collector, contacts and the active layer. Used printing equipment EKRA X1-SL and both screen printing with a screen mesh PET 1500 48-70 and stencil printing methods were tested. The electrolyte was printed 3 times, to obtain considerably a thick layer and completely cover the surface area of the previous layer, after each time cells were left to dry in the room temperature for 1-2 hours till completely dry before printing another electrolyte layer.

7. Supercapacitor cells conjugation

Every cell had a printed (active) surface area of 50 mm x 50 mm (Fig. 15). Cells of each substrate were prepared in dry state and by placing a thin (16µm) PET film with cut empty space of 45 mm x 45 mm in between two identical printed half-cells. Assembled cells were laminated at 120 °C for 30 seconds with a COMET-400 Digital hot press. In total nine supercapacitors were made, three of each material: Glassine Krystal Standart paper (G2), Filter paper and Aluminium.

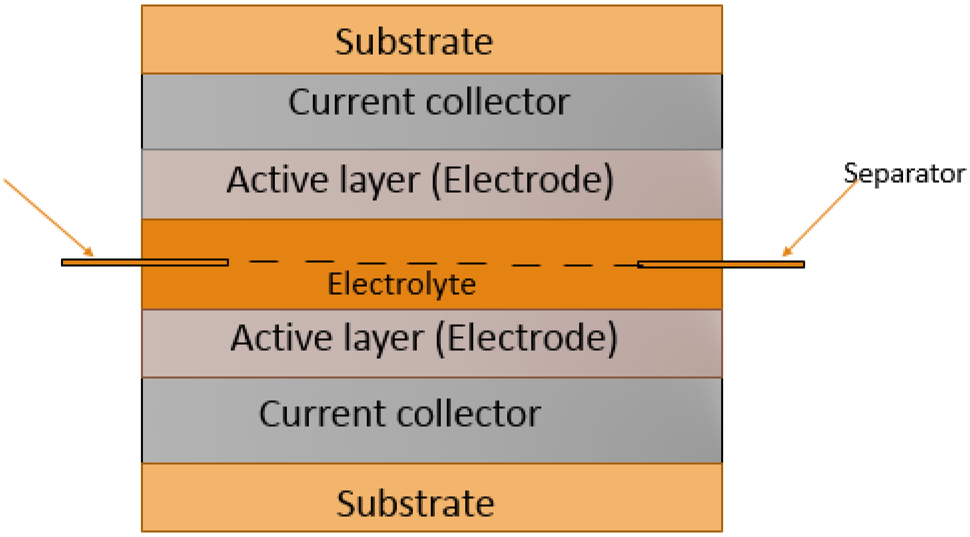

Figure 14 Scheme of printed supercapacitor

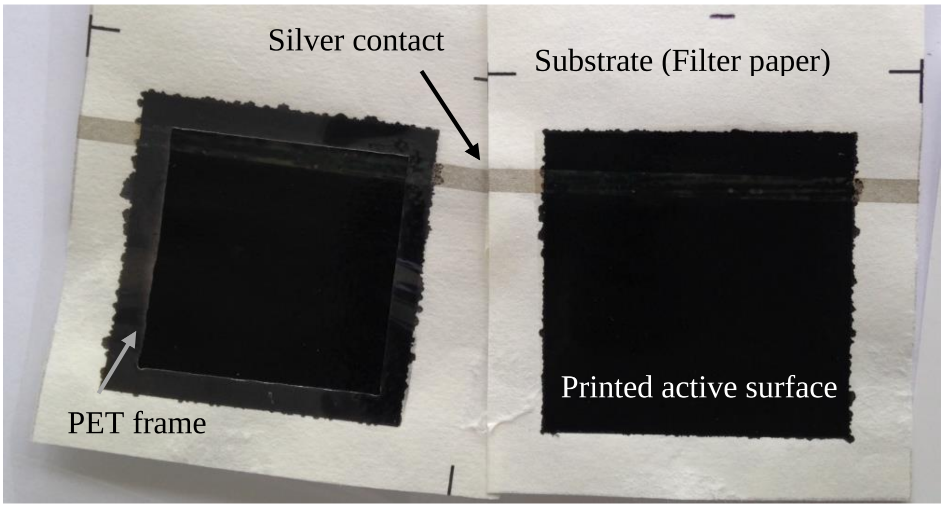

Figure 15 Two prepared supercapacitor hall-cells before lamination

Measurements

1. Viscosity measurements

Was made with Anton Paar Physica MCR 301 rheometer for all inks (AQ 0501, AQ 0301, CC, EMS, DP). Samples were measured using Parallel plates method leaving a gap (H) between plates 1 mm. The lower plate was heated until 25 ℃ temperature.

2. Layer thickness and surface roughness measurements

Layer thickness and surface roughness from printed inks were measured. These parameters were important for process continuity, it affects the size of the active surface area and also the adhesion with other supercapacitors layers printed subsequently. Layer thickness and surface roughness measurements were conducted with KEYNCE VK-9710 Laser Scanning Microscope mostly with 20 times or 50 times magnification. All samples used for these measurements were printed under same printing conditions, using screen mesh PET 1500 48-78 WPW. Only samples printed on PET substrate were used due to difficulties with removing the printed layer from other substrate surfaces. To proceed the measurement it was necessary to take off some of the printed layer from the substrate surface. To do it, very carefully thin needle was used to wipe or scratch printed ink from the top of the substrate.

Afterward to measure layer thickness from paper and aluminum samples Mitutoyo ABSOLUTE Digimatic Indicator was used. Measured used plain substrate, substrate with the collector, substrate with collector and active layer, substrate with collector, active and electrolyte layers. Then each layer thickness was calculated subtracting plain sample thickness from received values with certain printed layer.

3. Sheet resistance (resistivity) measurements

Sheet resistance measurement was made for all substrates printed with all inks. These measurements were conducted to find out which ink with which substrate interacts best and gives the minimum electrical resistance. The commercial four point probes instrument KEITHLEY 2612A with applied voltage of 200,000 mV and samples printed under same conditions with screen mesh PET 1500 48-78 WPW were used to proceed this sheet resistance measurement. After this measurement, the electrical resistivity was calculated for each ink film from equation

(3) $\rho = R * T$

where ρ – sheet resistivity, R- resistance, T- film thickness.

4. The electrical performance measurement

To calculate the capacitance of printed super capacitors the combination of two measuring methods was used. The capacitor, was charged with a constant voltage and discharged with a constant current. It was made using multimeter UNI-T UT61E as an amperemeter, multimeter VOLTCRAFT VC65OBT as a voltmeter and Programmable power supply device HAMEG HM8142 as power source. Supercapacitors were charged with ~1.2 V for 3 min and slowly discharged maintaining ~0.1 (0,098) mA current. Used circuits during charging and discharging are shown in Figure 16. Measurement data collected by using appropriate data processing software.

To calculate the capacitance of supercapacitor a segment from discharge curve was used. Also, it was estimated approximate full discharge time of capacitors. Calculations made from equations:

(4) $Ct = I\Delta t/\Delta V$

(5) $Td = \Delta V/\Delta t$

where Td – is full discharging time, Ct- Total capacitance, I is the constant current Δt- the discharging time corresponding to the specified potential change ΔV.

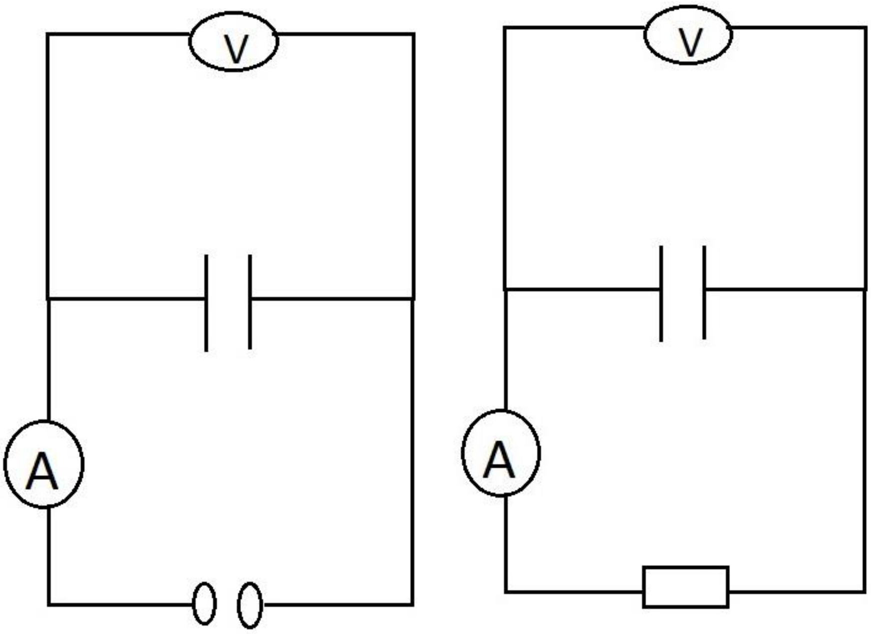

Figure 16 Circuits used to charge and discharge supercapacitors. On the left to charge, on the right to discharge

VIII. RESULTS AND DISCUSSION

Current collector selection

In order to have an acceptable capacity and reduce the resistance of supercapacitor (especially when non-conductive substrates are used as base), it is important to have a current collector, which ensures a good conducting path through the active material of the supercapacitor. Sometimes current collector also could be used as a physical support for the active material which otherwise would be fragile.

For the current collector selection, screen printing tests were made for five commercial carbon inks. All inks were tested using screen printing method with printing speed 150 mm/s. Also stencil printing method with a metal stencil printing form, printing speed 150 mm/s. Good ink interaction with the surface of the substrate it was printed on, achieved printed layer thickness per one printing time, ink's interaction with the printing process itself were important factors for the current collector layer. Firstly, to evaluate how ink behaves with printing processes as well as with used substrates visual observations were made. It was found that all used inks CC, EMS, DP except AQ0501, AQ0301 performed very well with both printing methods. The surface was covered nearly perfectly, despite which ink (CC, DP, EMS) on which substrate was printed, printed layer was smooth and even (Fig. 17). Also printing speed had no influence when printing with CC, EMS or DP inks. However, AQ0501 and AQ0301 mixtures gave unexpected and undesirable bubbly patterns on printed substrates (Fig. 18). This defect strongly occurred with screen printing and less with stencil printing method. Attempts to change the printing speed did not improve the quality, it was noticed that reducing the printing speed caused even more vivid and larger unwanted bubbles in the print out than printing with higher speed. Furthermore, it was noticed that AQ0501 mixture with ~5% concentration of Carbon nanotubes printing performance was better than AQ0301 mixture ~3%.

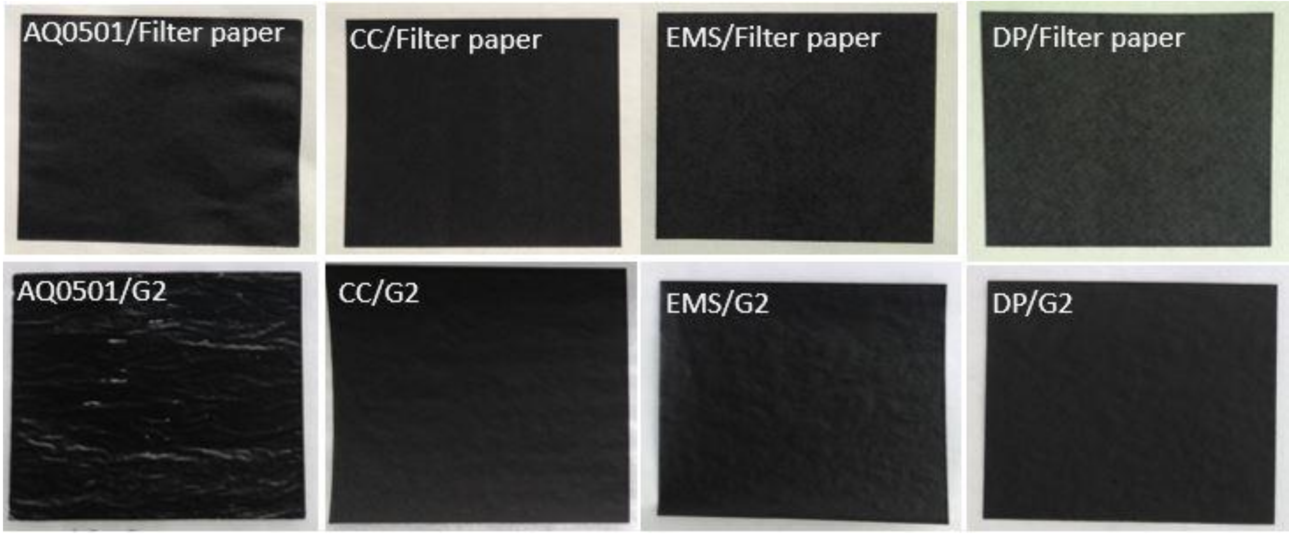

Figure 17 Printed samples with screen printing method, screen mesh PET 1500 48-70, printing speed 200 mm/s

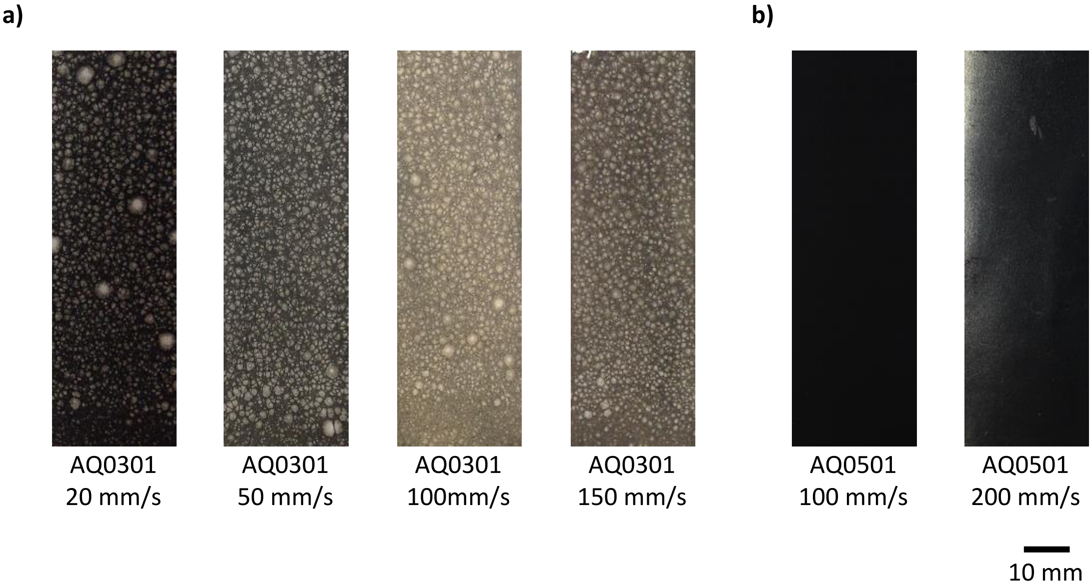

Figure 18 Samples printed with screen printing method, screen mesh PET 1500 120-34 YPW and different printing speed (a) AQUACYL 0501 (b) AQUACYL 0301

Active layer selection

In order to obtain higher specific capacitance and due to it is easy accessibility water based active and electrolyte materials were used in this work. When preparing active layer it was critical that used additives and solvents would help to reach a good printable texture and disperse carbon nanotubes. It was a great challenge to create mixture that works well with printing process and gives good and smooth printed layer. The main problem was to remove undesirable pattern, which was appearing when printing. Fifteen different mixtures with different material ratios were prepared and tested for the active layer (See Table 3). Firstly, it was intended to print all supercapacitor using only screen printing method, but after many attempts to print mixtures of different concentrations with screen printing, the unwanted pattern always appeared. Therefore stencil printing method was tested as well, which gave better results than screen printing. Founded, that most likely the foaming effect caused due to mixture going through the mesh. When stencil printing method was used to test mixtures unwanted pattern occurred, but significantly less (Fig. 19). The best printing results with the least visible pattern showed mixture Nr.15 and was chosen to be used as active layer material for printed supercapacitors.

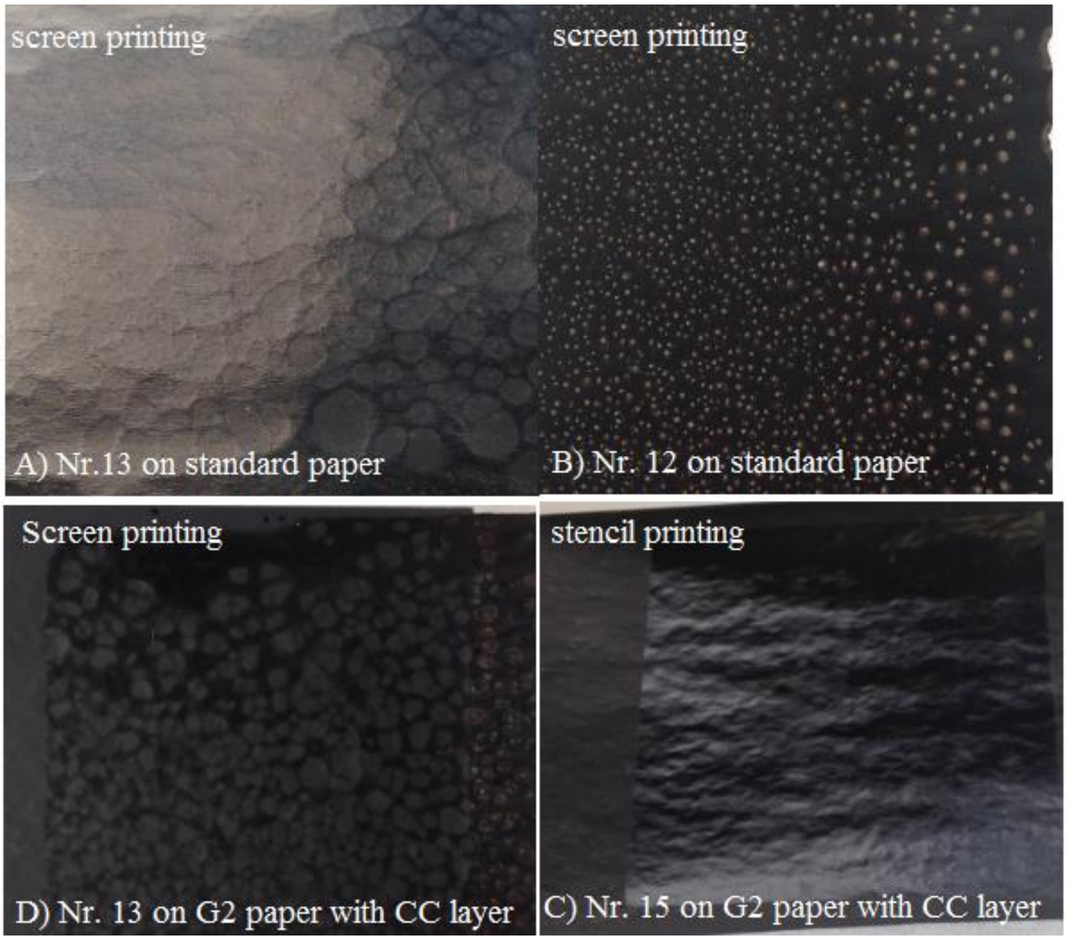

Figure 17 Printed active layer mixtures with different printing methods

Table 3 Composition of active layer mixtures

Mixture ID	Ratio			Percentage of solids (CNT), %	Additives
Mixture Nr.	(AQ0301)	PVA	H_3PO_4	Solids	
1	1	0	0	2,9	BYK-023, BYK -361N
2	1	0	0	2,9	BYK-023
3	1	1	1,5	2,1	
4	1	1	3	2,1	
5	1	1	1	2,4	BYK-023
6	1	1	1	2,6	
7	1	1	1	2,1	BYK-023
8	1	1	1	2,1	
9	1	1	1	2,1	
10	1	1	1	3,1	
11	1	1	1	3,2	
12	1	1	1	2,1	
13	1	1	1	4,3	
14	1	1	1	5,2	
15	1	1	1	5,3	

Electrolyte layer selection

As it was mentioned before, two different concentration mixtures for electrolyte layer were made mixing PVA with H_3PO_4 with a ratio 1:1 and 1:2. Mixtures were tested firstly with screen printing method, but unfortunately again foaming effect appeared due to mesh (Fig. 20. Fig. 21). Therefore, stencil printing method was tested as well, and gave much better results without any foaming traces.

Figure 18 Electrolyte (1:1) printed with screen printing method on G2 with carbon ink layer

Figure 19 Electrolyte mixture after printing with screen printing (using screen mesh)

Electrolyte printing tests were made on plain paper substrates also on printed carbon ink layers. It was found that electrolyte mixture interacts much better with carbon layer than with plain substrate. Some of printed samples were dried in the oven at 70 ℃ temperature for 5 min and at the same time some of samples were left to dry in a room temperature for 30 min (Fig. 22). Electrolyte mixtures printed on plain substrates and dried in the oven foamed, and the layer became few times thicker, and all structure from smooth became foamed, uneven and rough. It was assumed, that electrolyte reacts with some additives which are used in paper and with/in higher temperature the reaction was accelerated. Due to this reason decided to leave samples to dry in the room temperature. Electrolyte layer dried in the room temperature dried out nicely without any undesirable effects

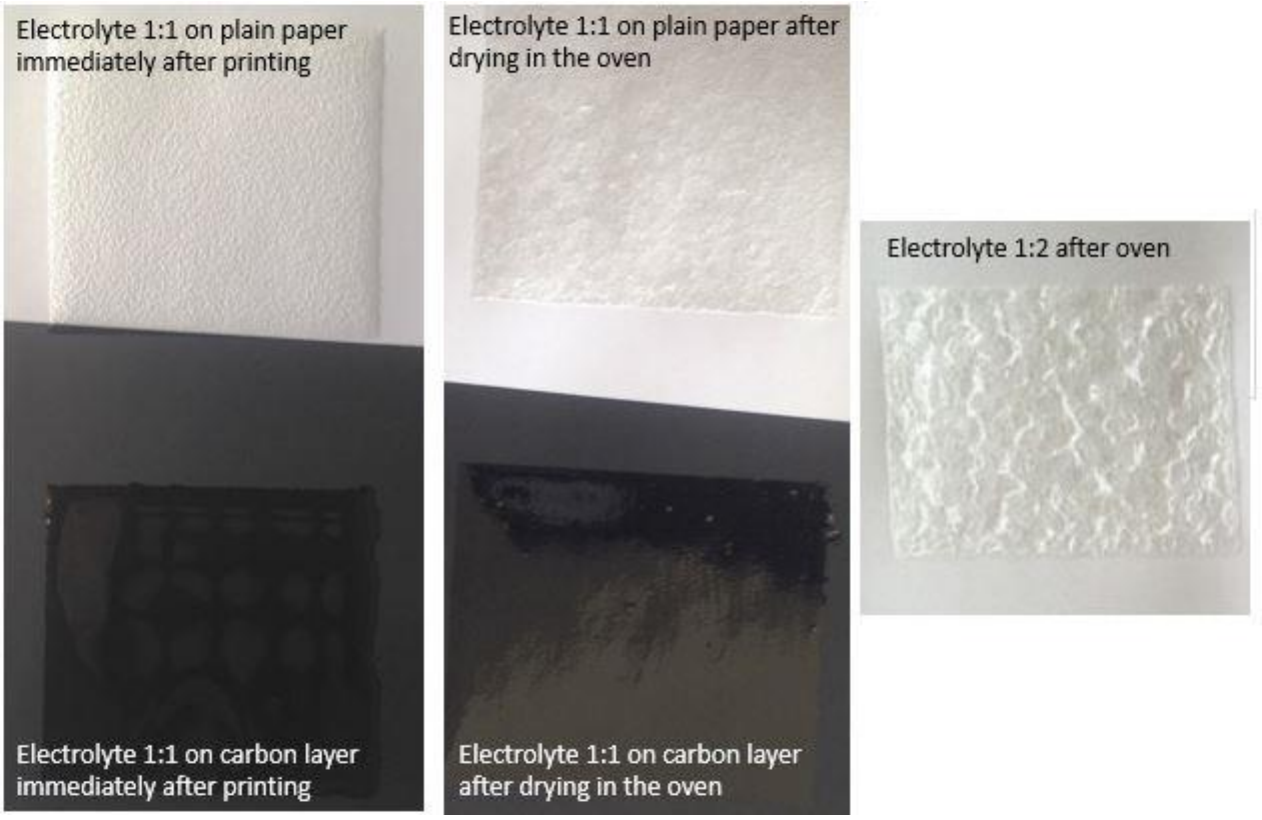

Figure 20 Behavior of electrolyte mixtures printed with stencil printing (immediately after printing and after drying in the oven at 70 C for 5 min.)

Viscosity

The viscosity is internal friction between molecules and particles when gliding along each other during a flow process or in other words its flow resistance. There are three main types of flow behavior (shown in Fig. 23):

- Ideally viscous (Newtonian). These fluids remain constant despite on temperature changes and the viscosity of such fluids remain constant when share rate changes;
- Shear-thinning (pseudoplastic). These fluids shows viscosity decrease when shear rate is increasing;
- Shear- thickening (dilatant). In such fluids viscosity increases with increasing shear stress.

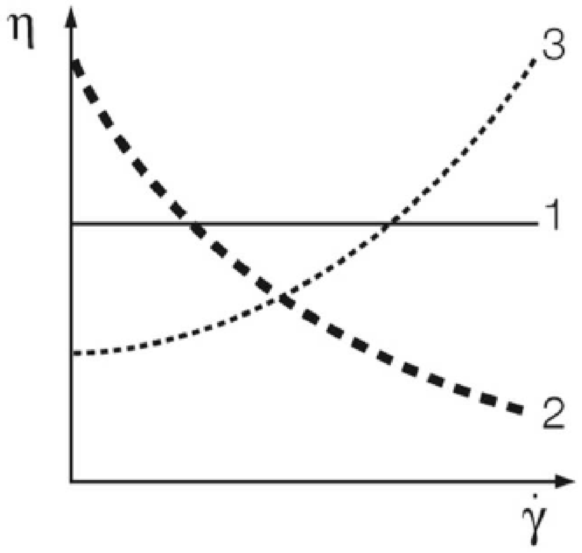

Figure 21 Flow behavior during coating, painting (printing) processes. Viscosity curves: 1-ideally viscous; 2-shear- thinning; 3- shear-thickening [21]

Figure 24 shows share rate versus viscosity curves of different inks. All measured inks shows share thinning behavior (pseudoplastic). The highest viscosity until share rate value was comparatively low showed CC ink which reached 534 Pa s, but at the highest share rate value (500 1/s) it became only 2,78 Pa s. Very similar behavior between each other showed DP and EMS inks. The highest viscosity values were 72,1 Pa s of DP and 101 Pa s of EMS - lowest 4,46 Pa s of DP and 3,06 Pa s of EMS. AQ0501 highest viscosity value was 42,8 Pa s and the lowest 0,13 Pa s. AQ0301 highest value was only 8,9 Pa s and the lowest 0,13 Pa s. AQ0501 and AQ0301 from the moment share rate reached value around 10 1/s behaved almost identically at higher share rate. Comparing with other three inks AQ0501 and AQ0301 showed more than 10 times lowest viscosity values at higher share rates, which can explain, why it was more difficult to print it with any of used printing methods, when all other inks were printed extremely well and without issues.

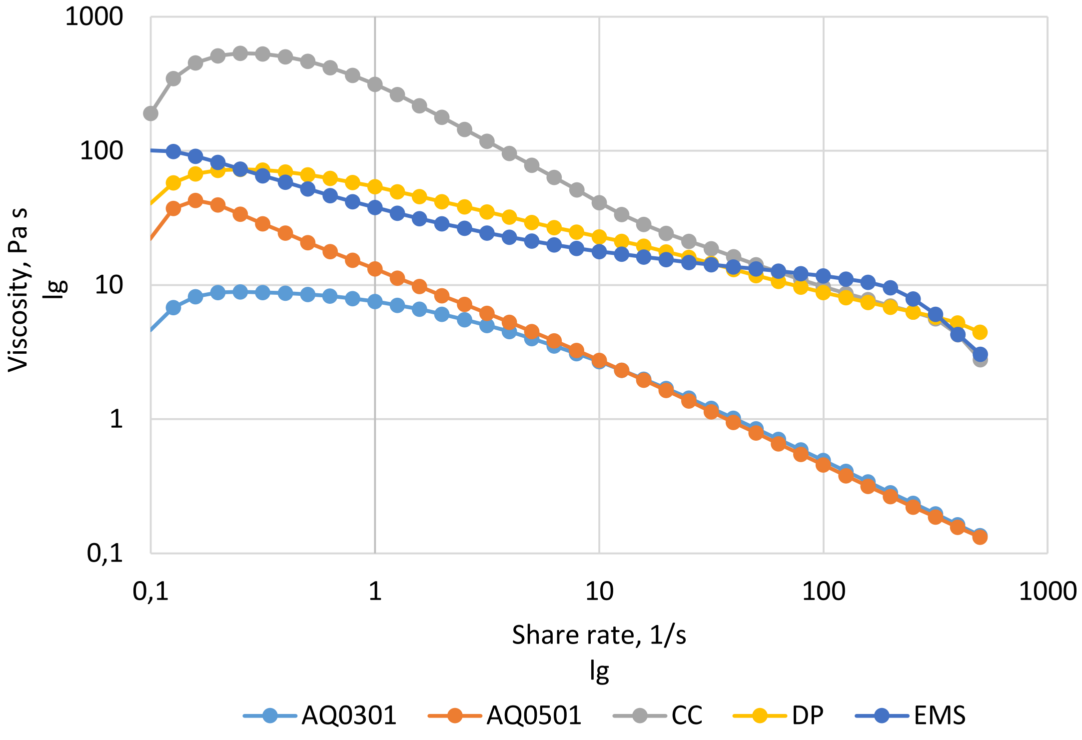

Figure 22 Share rate vs. viscosity of tested inks

Layer thickness and surface roughness of printed inks

Layer thickness measurements were done with samples printed on PET substrate with screen printing method, screen mesh PET 1500 48-70, printing speed 200 mm/s. Results showed that thickest layers obtained with Conductive Compounds C-200 Carbon Resistive Ink (CC) which was 13,9 μm. Du Pont 7105 Carbon conductive composition (DP) gave 8 μm thick layers, EMS Cl-1001 (EMS) 7,1 μm and AQUACYL 0501 Carbon nanotubes/water mixture (AQ0501) gave with 3,2 µm the thinnest layers (Fig. 25).

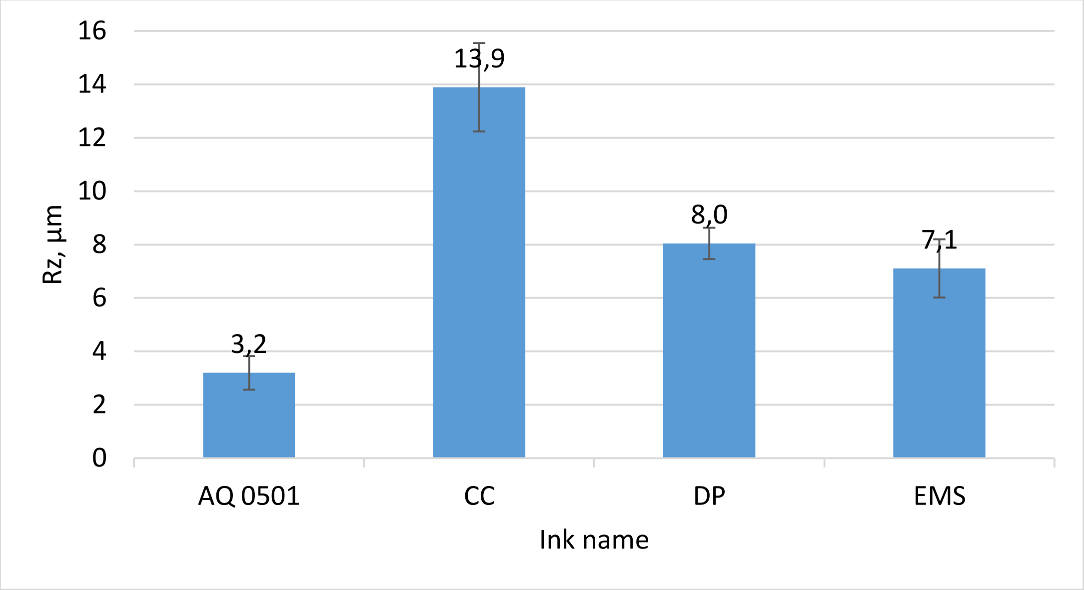

Figure 23 Printed layer thickness of different inks measured from PET samples printed with screen printing method, screen mesh PET 1500 48-70 WPW, 200 mm/s

Also, surface roughness measurement was carried out with same samples used to for layer thickness measurement. Surface roughness is important parameter and can lead to better final device performance such as capacity increase [20]. Fig. 26 shows that the highest maximum height of profile (Rz) had Du Pont 7105 ink 49,7 μm, slightly lower values had Conductive compounds C-200 Carbon Resistive Ink 44,9 μm and EMS Cl-2001 ink 40,9 μm.

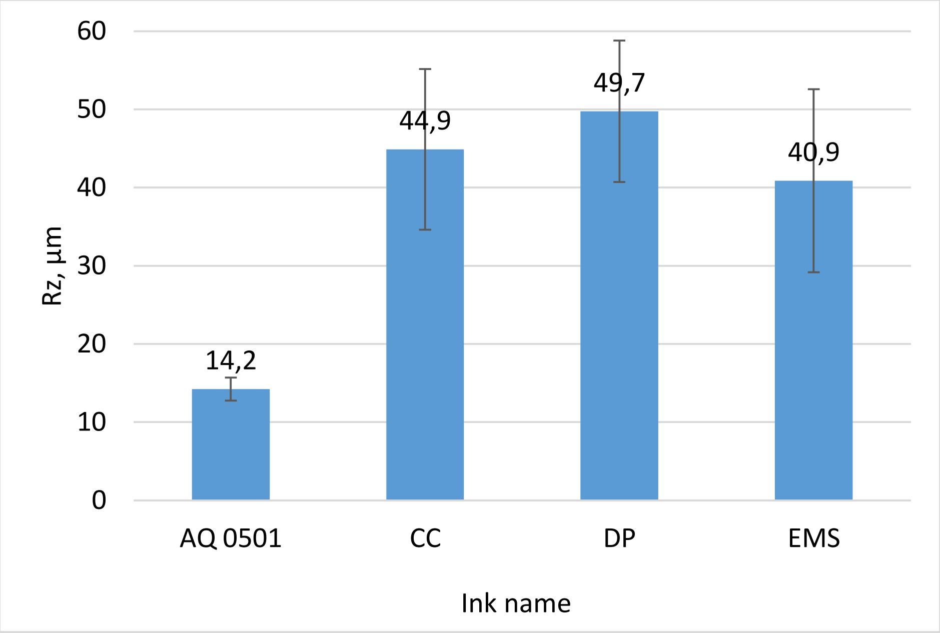

Figure 24 Maximum height of profile Rz of different inks measured from PET samples printed with screen printing method, screen mesh PET 1500 48-70 WPW, 200 mm/s

The lowest maximum height of profile showed AQUACYL 0501 mixture with 14,2 μm. Similar trend was observed with Arithmetical mean height (Ra) values. The highest value obtained by DuPont 7105 1,7 μm, Conductive compounds C-200 Carbon Resistive Ink and EMS Cl-1001 ink showed – 1,1 μm and AQ0501 – 0,2 μm (Fig. 27).

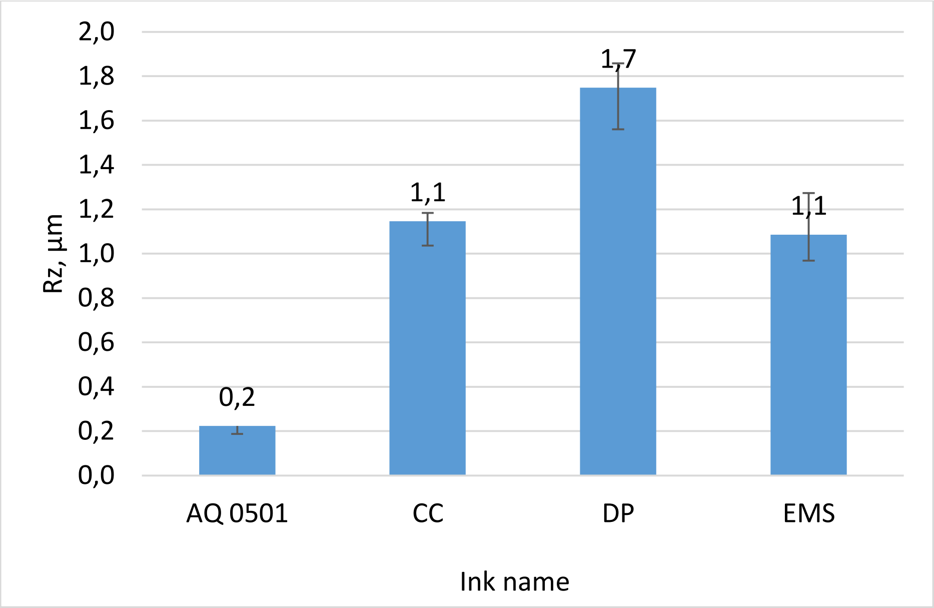

Figure 25 Arithmetical mean height Ra of different inks measured from PET samples printed with screen printing , screen mesh PET 1500 48-70 WPW, 200 mm/s

Sheet resistance of printed inks

Electrical sheet resistivity measurements were made for each substrate with each ink (Fig. Nr. 26). Measurement was made using samples printed with screen mesh PET 1500 48-70 WPW. CC ink showed the best performance independent on which substrate (conductive or isolator) it was measured, all values were very low and similar in a range from 20 to 40 Ω only filter paper showed little bit higher resistivity which was 76,6 Ω. Values of AQ0501 were in a range from 80 to 180 Ω, Zinc coated paper and all Glassine papers (G1, G2, G3) showed very similar values in a range from 80 to 100 Ω, The highest value were obtained by PET samples -107,8 Ω and the lowest – 83,3 Ω by G2 paper. Aluminium as a conductive substrate showed comparably high resistivity – 159,1 Ω this could have happened due to poorly stirred AQ0501 ink before printing samples and making AQ0501 ink have less carbon nanotube particles, comparing with results from samples printed with same ink on other conductive substrate Zinc coated paper printed another time and stirring mixture better before printing. DP ink gave sheet resistivity values in a range from 50 to 440 Ω. The lowest value - 51,1 Ω was measured on Aluminum samples and the highest 443 Ω on filter paper samples. Extremely high values with each substrate showed EMS ink. The lowest value 1423 Ω was obtained from Zinc coated paper samples, the highest – 21583 Ω from PET samples.

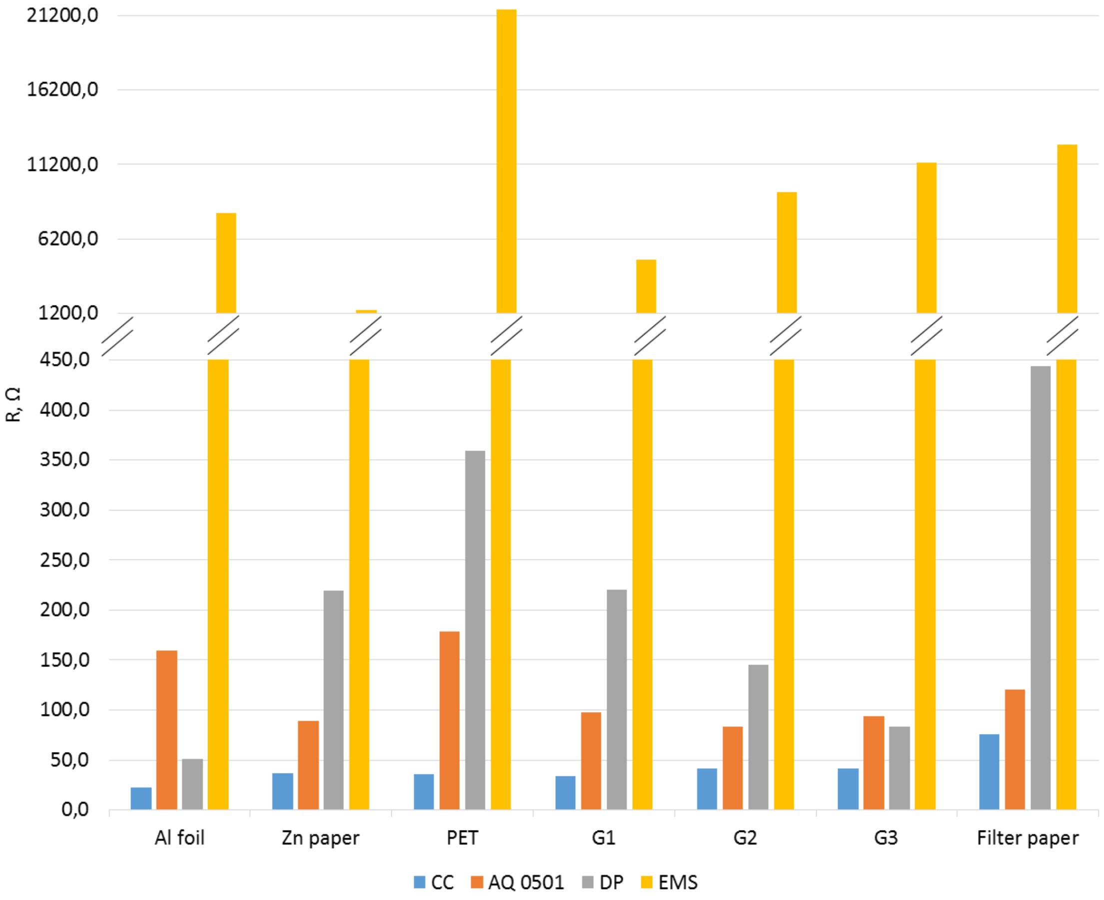

Figure 26 Sheet resistivity of inks printed under same conditions with screen printing method, screen mesh PET 1500 48-70 WPW

It is important to mention that these results are depended on layer thickness. To have a better understanding, the resistance of each ink was calculated using obtained results from electrical sheet resistivity and layer thickness measurements (Table 4).

Table 4 Resistance values of each ink with different substrate calculated from sheet resistivity and layer thickness results.

Ω/µm	**Al foil**	**Zn paper**	**PET**	**G1**	**G2**	**G3**	**Filter paper**
CC	309,0	508,4	499,2	475,2	574,9	579,4	1050,3
AQ 0501	508,4	284,9	571,3	312,0	265,8	299,9	384,7
DP	179,0	294,4	289,1	275,2	333,0	335,6	608,3
EMS	56495,2	10110,9	153311,2	34183,6	66481,5	80269,8	88933,7

After evaluation of received results from printed layer thickness, electrical resistance, surface roughness measurements, it was decided to use CC ink as a collector layer because it gave the thickest layer and comparing good sheet resistance values and it seemed the best choice for the collector layer.

Thickness of printed collector, active and electrolyte layers

Each layer of half-cell were measured with Mitutoyo ABSOLUTE Digimatic Indicator. From measured results the approximate thickness of each printed layer on the cell was calculated subtracting one layer values from another. Where average value from all measured substrates of collector layer was 11,3 µm, of active layer 6 µm and of electrolyte 39,7 µm. More detailed values from measurements, and calculations from each used substrate are given in the Table 5. And how the surface looks covered with each material shows Fig. 29.

Table 5 Layer thickness of printed supercapacitor layers

Layer thickness, µm			
Substrate	Aluminum	Filter paper	Glassine paper (G2)
Plain	76	129	21
Standard Deviation	4	8	3
With Collector (Conductive compounds C-200)	85	141	34
Standard Deviation	2	7	2
With Collector and Active layer	88	150	40
Standard Deviation	2	6	4
With Collector, Active and Electrolyte layers	128	187	82
Standard Deviation	5	6	7
Collector layer	9	12	13
Standard Deviation	2	0	1
Active layer	3	9	6
Standard Deviation	2	2	0
Electrolyte layer	40	37	42
Standard Deviation	0	2	2

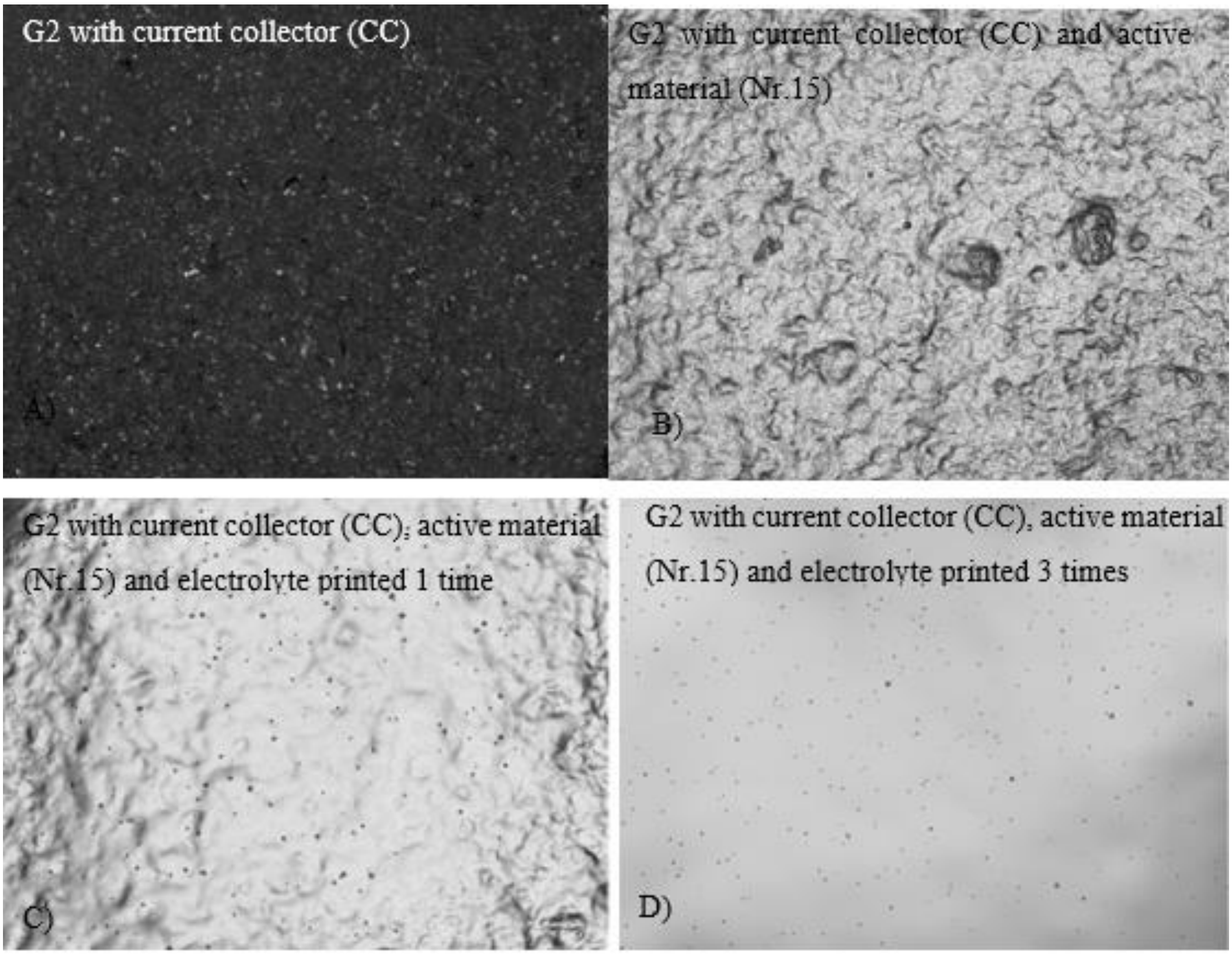

Figure 27 Printed layers: G2 with: printed current collector (A), printed current collector and active layers (B), current collector, active layer and electrolyte layer printed 1 time (C), current collector, active layer and electrolyte layer printed 3 times (D)

To have better feeling how all layers interacted with each other also to have visual observation about layers thickness the cross-section images were taken with a help of laser scanning microscope (Fig 30, Fig. 31).

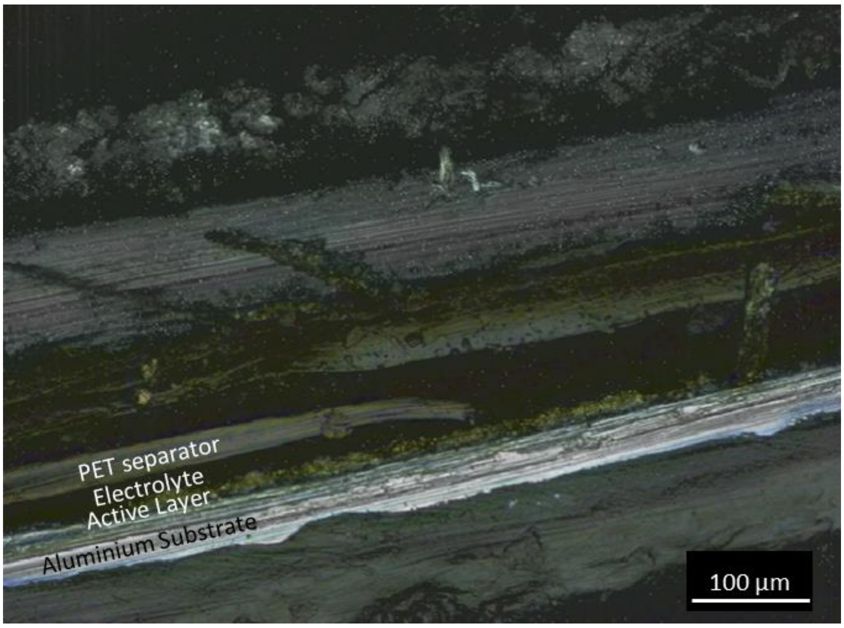

Figure 28 Cross-section of supercapacitor made with aluminum substrate

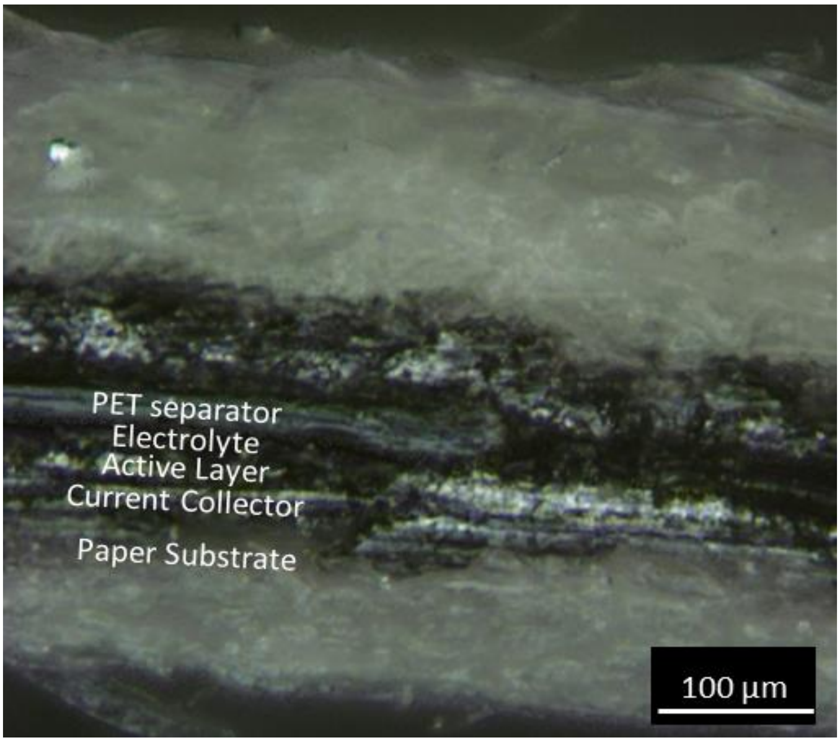

Figure 29 Cross-section of supercapacitor made with filter paper substrate

Supercapacitors electrical performance and capacitance calculations

Assembled supercapacitors electrical performance estimation reflected in Fig. 32, which shows the average performance of supercapacitor, made with different substrate. Charging period is shown from -50 s till 0 s (as it was mentioned before that charging process was kept for 3 min, but since discharging current used for calculations, only a segment of charging is shown in the graph). Charging was conducted with a constant voltage 1,2 V. During charging the Al showed lowest current value ~0,05 mA which was comparably better and gave smaller loses in the system than G2 and Filter paper where value was ~0,14 mA. Also it can be claimed that all capacitors were fully charged because the current was constant these last 50 s of charging. Discharging was maintained with a constant current value 0,1 mA where very similar behavior showed capacitors from Al and G2 their discharging time was nearly two times longer comparing with Filter paper. The capacitance of Aluminum and Glassine paper was also almost 2 times greater than Filter paper. Also for curiosity, it was estimated that full discharge time would take: 144,3 s for filter paper; 258,8 s for glassine paper and 261,3 s for aluminum supercapacitor.

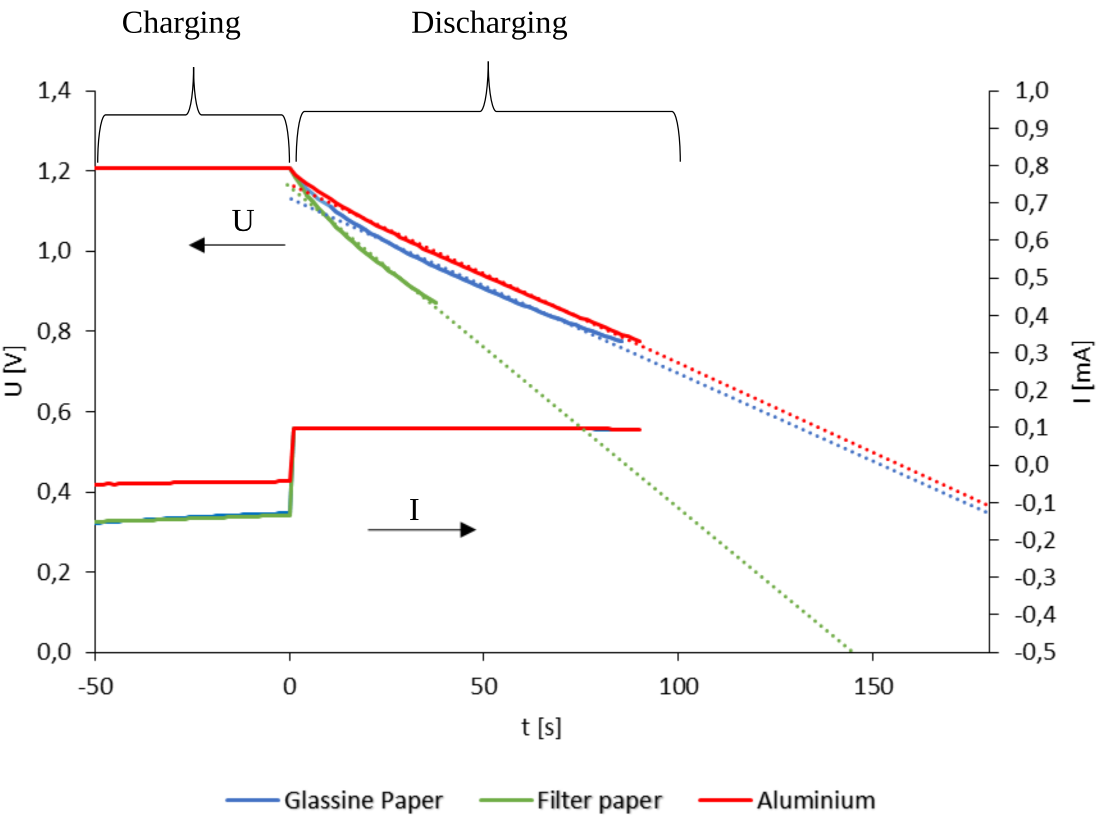

Figure 30 An illustration of supercapacitors measurement results with linear Voltage change over time

Table 6 Calculated values of printed supercapacitors performance

Quantity	Units	Filter paper	Aluminum	Glassine paper (G2)
Capacitance	mF	12,3	21,9	22,5
Cell weight	g	1,0	1,3	0,6
Capacitance per gram	mF/g	12,3	16,9	37,5
Capacitance per square centimeter	mF/cm^2	0,6	1,1	1,1

IX. CONCLUSIONS

- Fully functional supercapacitors can be efficiently manufactured by conventional printing technologies such as screen printing and stencil printing.
- Paper which, is very cheap and light material can be used as substrate and carbon nanotubes as active component as well as phosphoric acid (with PVA), which makes this device to be cheap and much more environment friendly comparing with conventional supercapacitors.
- From tested inks best performance fur current collector showed Conductive compounds C-200 Carbon resistive Ink.
- Best active layer mixture was Nr.15, which had the highest percentage of solids (CNT).
- From produced supercapacitors the best performance (capacitance) showed G2 (Glassine Krystal Standard paper) which reached 22,5 mF per cell and 37,5 mF/g (including weight of all device).

Further work

In order to understand, if layer thickness of active layer and electrolyte has influence to supercapacitors capacitance there could be done, further investigations. Where could be done more capacitors with different layer thickness of active layer and then of electrolyte. It would be interesting to know if electrolyte composition (concentration of acid) has any influence for electrical device performance. To do this, there could be made supercapacitors under same conditions but with electrolyte mixture 1:2. Moreover, further investigation could be done to estimate if occurring bubbly pattern when printing active layer materials has any effect on supercapacitors performance. Also there could be done adjustments and tests to adopt this supercapacitors printing concept for gravure printing method.

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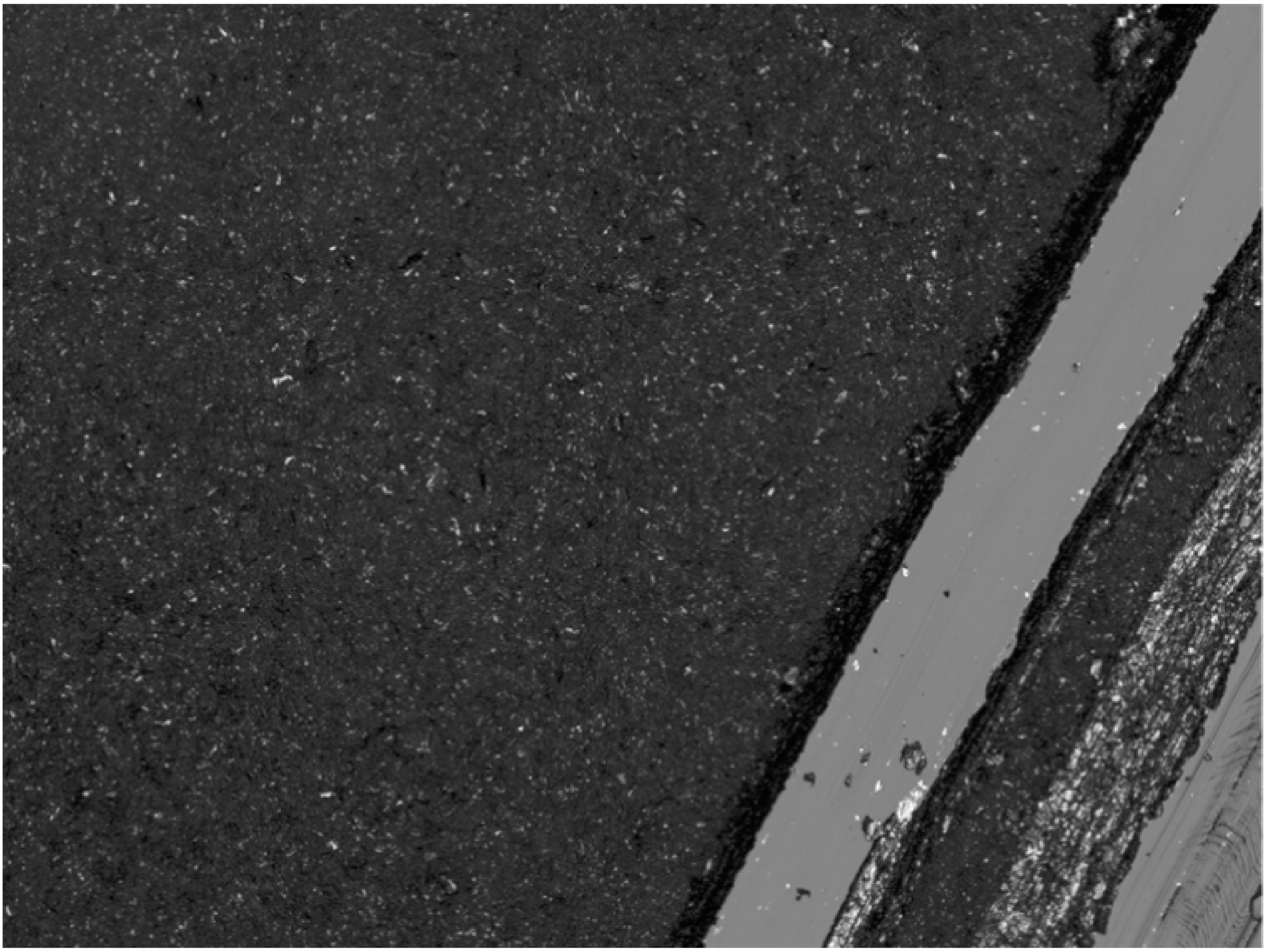
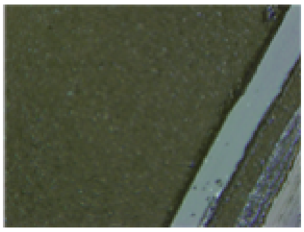
PET CC 2.rpt

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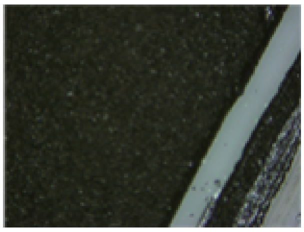
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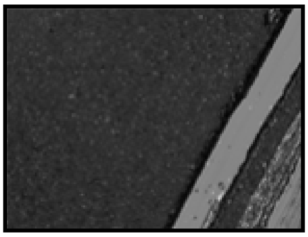
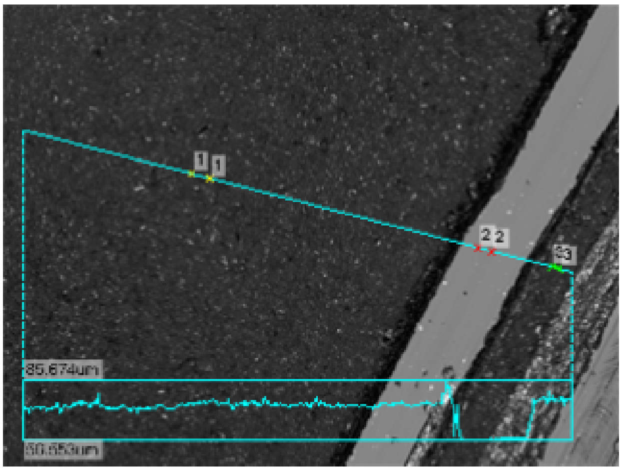
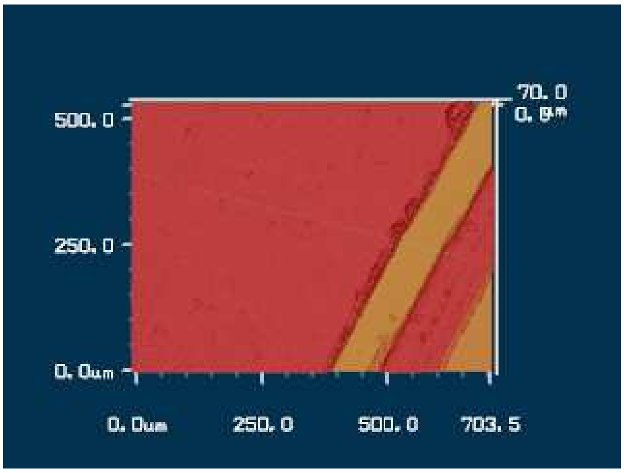
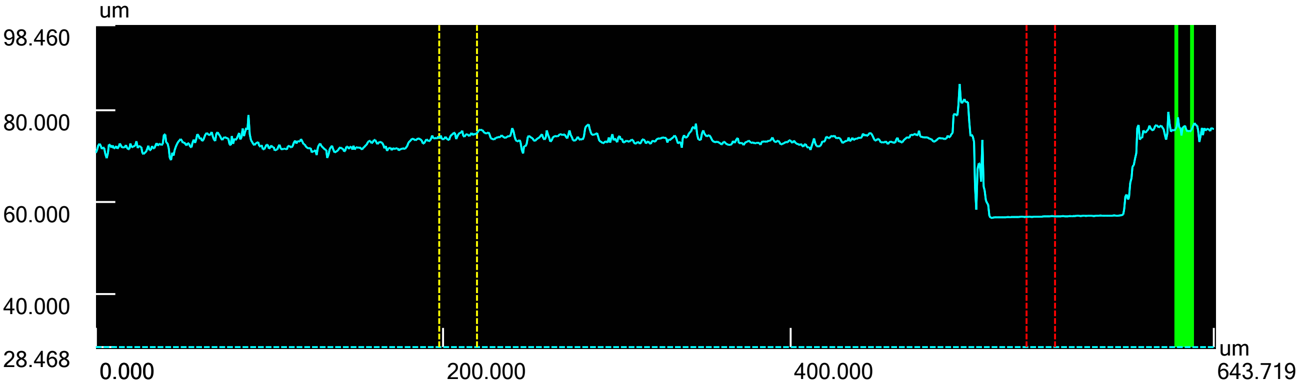

Laser intensity


Height

Profile



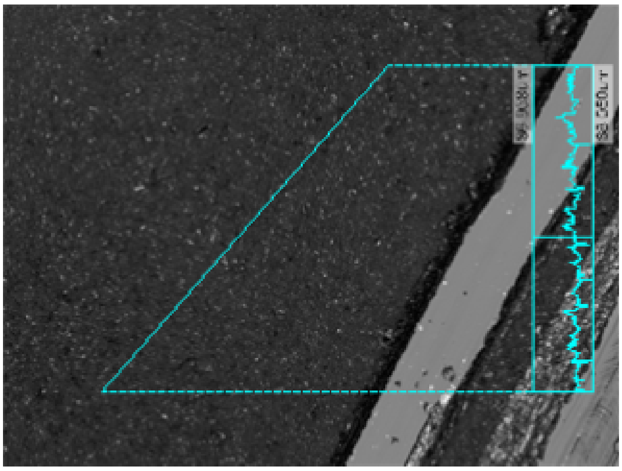


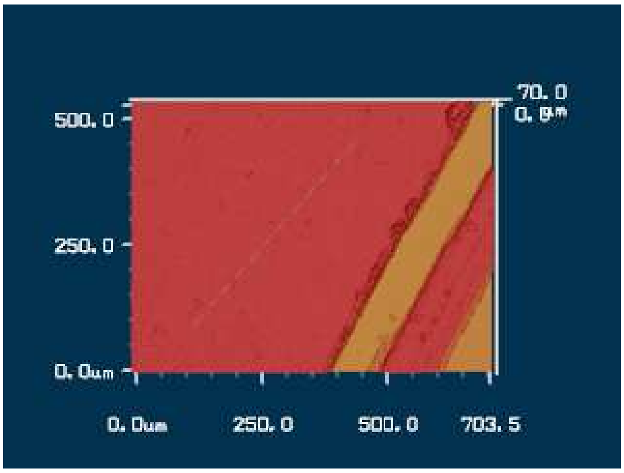


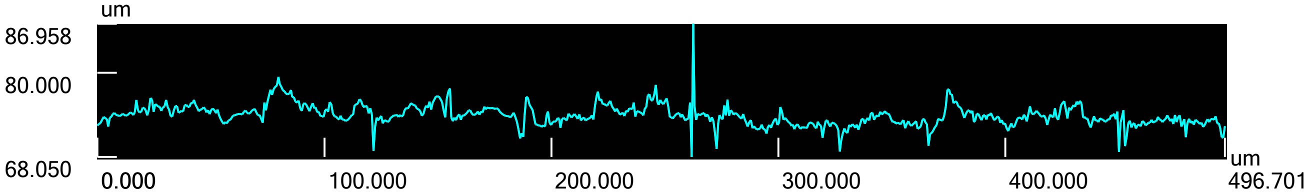
Profile1	Horz. dist.	Hght. diff.	Hght. ave.	Angle	C.S. length	C.S. area	R	Comment
All	643.719um	5.213um	71.367um	0.464°	873.666um	27644.199u...		
Seg.1	21.729um	0.719um	74.438um	1.894°	25.770um	1010.611u...		
Seg.2	16.297um	0.152um	56.840um	0.535°	16.305um	467.796um2		
Seg.3	9.054um	0.183um	76.014um	1.157°	15.485um	457.302um2		
Seg.4								
Seg.5								
Seg.6								
Seg.7								
Seg.8								
Seg.9								
Seg.10								
Total	47.079um	1.054um	207.293um	3.587°	57.560um	1935.709u...		
Max.	21.729um	0.719um	76.014um	1.894°	25.770um	1010.611u...		
Min.	9.054um	0.152um	56.840um	0.535°	15.485um	457.302um2		
Ave.	15.693um	0.351um	69.098um	1.196°	19.187um	645.236um2		
Std. DV	5.192um	0.260um	8.691um	0.555°	4.667um	258.394um2		
3sigma	15.577um	0.780um	26.074um	1.666°	14.002um	775.183um2		

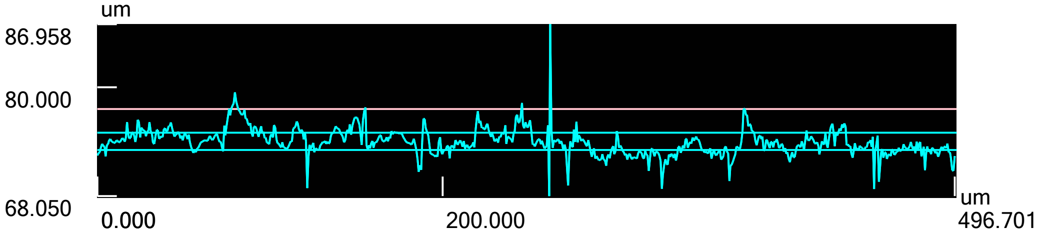
Profile1
Correction : Smooth intensity None, DCL/BCL None, Smooth height None, Correct tilt None
Ref. value1 : 98.460um
Ref. value2 : 28.468um
Step : 69.992um

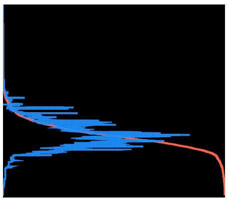
Line roughness











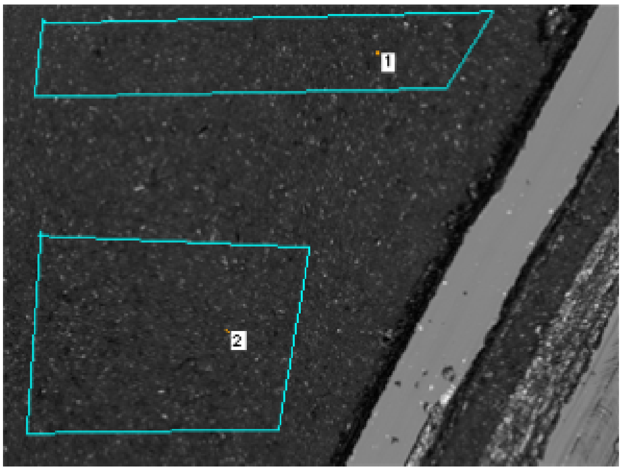
BAC/ADF

Profile 1	Rδc	Rmr	Rmr(c)	RPc	RHSC	Rk	Rpk	RMr1	RA1	Rvk	RMr2	RA2	Comment
All	1.639um	50.00%	0.00%	11pieces	7pieces	2.941um	1.955um	14.68%	14.347um%	1.447um	91.45%	6.184um%	
Parameter1	Ref. mr=25.00%	Ref. mr=50.00%	Cut level=0.000um	D.Z. width=5.00%	Cut level=50.00%								
Parameter2	Comp. mr=75.00%	Lvl. diff=0.000um											

Profile 1	Horz. dist.	Rp	Rv	Rz(Rt)	Rc	Ra	Rq	Rsk	Rku	RΔq	RSm	RPc/cm	RLo	Rlr	R▯a	Rλa	R▯q	Rλq	Comment
All	496.701um	12.972um	5.937um	18.909um	8.059um	1.063um	1.478um	1.0063	11.9178	1.3642	115.244um	86.772	720.359um	1.4503	30.25°	12.652um	36.45°	14.593um	
Seg.1																			
Seg.2																			
Seg.3																			
Total																			
Max.																			
Min.																			
Ave.																			
Std. DV																			
3sigma																			

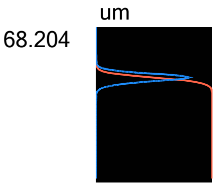
Profile 1
Correction : Smooth intensity None, DCL/BCL None, Smooth height None, Correct tilt None
JIS B0601:2001(ISO 4287:1997)
Cutoff : Roughness λs None, λc None

Surface roughness

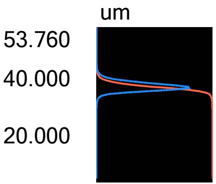


	Rp	Rv	Rz	Ra	Rq	Rsk	Rku	Rδc	Rmr	Rmr(c)	Comment	Rδc ref....	Rδc Co...	Rmr ref....	Rmr lvl....	Rmr(c) c...
Seg.1	23.316um	44.888um	68.204um	1.478um	1.960um	-0.8098	21.1995	2.412um	50.00%	99.97%		25.00%	75.00%	50.00%	0.000um	34.102um
Seg.2	21.461um	32.299um	53.760um	1.197um	1.626um	0.1579	12.2866	1.893um	50.00%	99.69%		25.00%	75.00%	50.00%	0.000um	26.880um
Seg.3																
Seg.4																
Seg.5																
Seg.6																
Seg.7																
Seg.8																
Seg.9																
Seg.10																

	Rp	Rv	Rz	Ra	Rq	Rsk	Rku	Rδc	Rmr	Rmr(c)	Comment
Total	44.776um	77.188um	121.964um	2.675um	3.586um	-0.6519	33.4860	4.305um	100.00%	199.66%	
Max.	23.316um	44.888um	68.204um	1.478um	1.960um	0.1579	21.1995	2.412um	50.00%	99.97%	
Min.	21.461um	32.299um	53.760um	1.197um	1.626um	-0.8098	12.2866	1.893um	50.00%	99.69%	
Ave.	22.388um	38.594um	60.982um	1.337um	1.793um	-0.3259	16.7430	2.152um	50.00%	99.83%	
Std. DV	0.927um	6.295um	7.222um	0.141um	0.167um	0.4839	4.4564	0.259um	0.00%	0.14%	
3sigma	2.782um	18.884um	21.666um	0.422um	0.502um	1.4516	13.3693	0.778um	0.00%	0.42%	



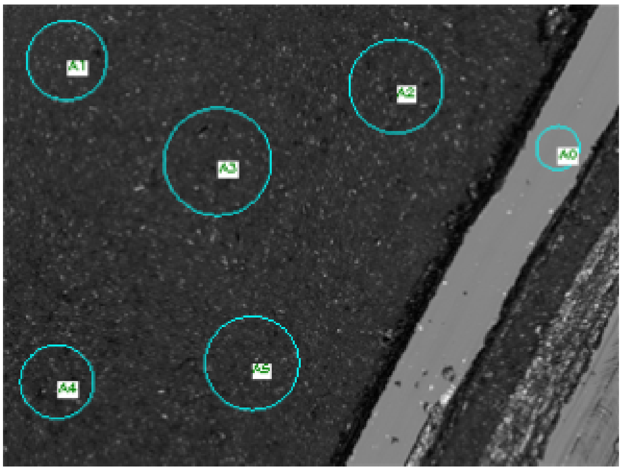
BAC/ADF(#1)



BAC/ADF(#2)

JIS B0601:2001(ISO 4287:1997)
Cutoff : Roughness λs None, λc None

Average step



Measure A	Seg.	Step	Ave. height	Min. height	Max. height	Comment
0(Ref.)	2pt. circ.		56.929um	56.687um	57.329um	
1	2pt. circ.	14.175um	71.104um	28.909um	93.489um	
2	2pt. circ.	17.898um	74.827um	33.748um	96.672um	
3	2pt. circ.	16.292um	73.221um	34.511um	85.494um	
4	2pt. circ.	15.734um	72.663um	41.085um	90.801um	
5	2pt. circ.	16.696um	73.625um	41.345um	85.718um	
Total		80.794um	422.368um	236.285um	509.503um	
Max.		17.898um	74.827um	56.687um	96.672um	
Min.		14.175um	56.929um	28.909um	57.329um	
Ave.		16.159um	70.395um	39.381um	84.917um	
Std. DV		1.220um	6.124um	8.863um	12.964um	
3sigma		3.661um	18.373um	26.590um	38.891um	

Measure B	Seg.	Step	Ave. height	Min. height	Max. height	Comment
0(Ref.)						
1						
2						
3						
4						
5						
Total						
Max.						
Min.						
Ave.						
Std. DV						
3sigma						