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Impact of Calendering and Silver Addition to Carbon Nanotube-Based Electrodes Used in Printed Multi-Layer Capacitors

Ramea Awni Al-Mubarak
Western Michigan University, ramea.awni@gmail.com

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IMPACT OF CALENDERING AND SILVER ADDITION TO CARBON NANOTUBE-BASED ELECTRODES USED IN PRINTED MULTI-LAYER CAPACITORS

by

Ramea Awni Al-Mubarak

A thesis submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Master of Science
Paper and Chemical Engineering
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August 2015

Thesis Committee:

Margaret Joyce, Ph.D., Chair
Dan Fleming, Ph.D.
Thomas Joyc, Ph.D.
As the demand for global energy increases, the need for development of alternative clean and sustainable energy technology increases. Creating advanced energy devices with a large storage capacity plays a significant role in this development. This research focused on investigating the performance of capacitor devices used as energy storage cells by optimizing and determining the impact of silver percentage and structure (nano-wires or silver flake) added to CNT ink on the conductivity of printed layers, and studying the influence of calendering the multi-layer capacitor electrodes. Multi-layer capacitors were fabricated by screen printing three alternative layers of conductive and dielectric inks on top of each other onto a polyethylene terephthalate (PET) substrate. Also, a graphite ink was fabricated and the effect of adding silver flake to this ink was studied. The optimum silver percentage in the CNT ink was found to be 3 wt.% nanowires. Results also showed that calendering did not improve the conductivity of the CNT printed sheets.
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Ramea Awni Al-Mubarak
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CHAPTER 1
INTRODUCTION

The demand for global energy is growing at an unsustainable rate. Energy supply depends mainly on the use of fossil fuels, which are decreasing significantly and becoming increasingly expensive. According to the United States Department of Energy, the world’s energy consumption will increase by 20% in 20 years [1]. In addition, fossil fuel extraction, transport and consumption have an environmental impact, due to the associated emissions of greenhouse gases and other toxic pollutants. The growing concerns over the increasing demand for fossil fuels and their effect on the environment have supported research on sustainable and renewable energy development. After energy harvesting, the energy produced also needs to be stored until required for use and used more responsibly. The main objective is hence the minimization of energy loss during storage and creating advanced energy storage devices with large storage capacity. Batteries and supercapacitors have been recognized as the most important devices among all energy storage technologies [2]. Thus, research focusing on improving the performance of supercapacitors is necessary. To create advanced supercapacitors to help alleviate the energy storage predicament, engineering improvements and substantial progress in research are needed. The objectives of this research are to optimize and to determine the impact of silver percentage and structure (nano-wires or silver flake) added to CNT ink on the conductivity of printed layers, The optimum conductive ink blend will then be used to screen print the electrode layers of multi-layer capacitors. The capacitors will be fabricated by printing alternative layers of dielectric and CNT blended ink on top of each other on a polyethylene terephthalate (PET) substrate. The influence of
calendering the multi-layer capacitor electrodes on its conductivity and surface topography will be studied. The performance of these capacitor devices will be measured and compared. Finally, a graphite ink will be fabricated and its bulk conductivity compared with the commercial CNT ink used for this research.
CHAPTER 2

LITERATURE REVIEW

Electrical energy can be stored in two major types of energy storage devices: batteries and capacitors, which are the main storage devices that store energy in completely different ways. Batteries have two electrical terminals, electrodes, separated by an electrolyte, which is the chemical substrate in which the chemical energy is stored. Batteries directly convert the chemical energy stored in the electrolyte to electrical energy through chemical reactions, oxidation and reduction, that occur at both electrodes. The generated charge creates a voltage between the two terminals, the electrodes. Once the chemicals have all been depleted, the redox reactions stop and the battery is dead [3]. Energy is stored in capacitors through charge separation, whereby static electricity between two oppositely charged plates is used rather than chemistry to store the energy [3]. Inside a capacitor, there are two conducting metal plates separated by an insulating material termed a dielectric. During charging, negative and positive electrical charges build up on the plates, which are separated by the dielectric that prevents the plates from coming into contact with each other. The dielectric layer can be a solid material or an ionic solution. It may be made of something like mica (a ceramic), a thin plastic film, paper, quartz, ethanol, glycol, or even simply air [2]. When forming a closed circuit between the two electrodes, the electrical potential is released forming a power density [4]. Capacitors have two main functions: blocking the flow of the direct current, DC, and charging or discharging electricity. That is why they are used to filter the output in a power supply so there is little perturbation in the current. In general, a capacitor acts like a filter, where it blocks lower frequencies and passes higher ones [4].
2.1 Comparison Between Batteries and Capacitors

Electrical energy storage device performance can be compared in terms of power and energy density. Generally, the measure of how fast the energy is transferred to a device per unit mass is called power density, $J/(Kg\ s)$. Energy density is the amount of energy stored in unit mass, $J/Kg$ [5]. Batteries have higher energy density, in other words they can store more energy per unit mass. But, capacitors have a higher power density, which means they can release energy faster. This is why batteries are still the best option for storing large amounts of energy over long periods of time, while capacitors are more suitable for storing and releasing large amounts of power relatively quickly. In theory, capacitors have many advantages over batteries: they weigh less, in general they do not contain harmful or toxic chemicals, the cycle efficiency (which is the ratio of discharge energy output of the capacitor over the charge energy input at each cycle, which will increase as the energy loss due to the existing equivalent series resistance (ESR) decrease) can be above 95%, and they can be charged and discharged millions of cycles, while batteries can only be charged and discharged thousands of cycles, which means the lifetime of batteries is finite. This could be a significant problem when a battery is placed in a permanent structure, such as a biomedical implant, an engine, or a concrete support structure [6].

2.2 Supercapacitors

Scientists are now developing a new technology that combines the main advantages of capacitors and batteries; these devices are termed supercapacitors. Supercapacitors are designed to work as capacitors, but they are also designed in a way to enable them to
store a significant amount of energy. A supercapacitor, also called an ultracapacitor, or an electrochemical capacitor (ECC), differs from a conventional capacitor in two main ways: its plates effectively have a much larger area because of the nature of the electrode construction material and the distance between the two plates, the electrodes, is much smaller. A supercapacitor, as an ordinary capacitor, has two plates, electrodes, which are separated by a dielectric. The electrodes are made of a porous substance with high surface area per unit mass such as activated carbon, multi- and single-wall carbon nano-tubes, graphene, etc. [7].

Conventional capacitors such as electrostatic and electrolytic capacitors cannot fulfill the needs of today’s computer world [8]. The yield capacitances of electrostatic capacitors are in the range of 0.1 to 1 μF with a voltage range of 50 to 400 V [8]. Electrolytic capacitors are next generation capacitors: they are made of tantalum, aluminum, and ceramic electrolytic capacitors. The capacitances of electrolytic capacitors are in the range of 0.1 to 10 μF with a voltage profile of 25 to 50 V [8]. Ceramic capacitors consist of alternating layers of metal (electrode) and ceramic (dielectric). Multi-layer ceramic capacitors (MLCs) consist of around 100 alternating layers of metal and ceramic fabricated by screen-printing metal layers onto ceramic layers. For usable capacitance, every even metal layer must be in electrical contact with one another and every odd layer must be in electrical contact with one another, so that there are only two electrodes and an effectively large surface area of thin ceramic dielectric. The capacitance range of ceramic capacitors is normally the same as the capacitance range of Ta and Al electrolytic capacitors (10 μF). Ceramic capacitors are very useful in high frequency applications [8]. Electrochemical capacitors are the next generation of capacitors and
there are two main types of electrochemical capacitors: electric double layer capacitors (EDLC), and pseudocapacitors [8]. EDLCs fill the gap between batteries and conventional capacitors, since they are able to give greater energy densities than the conventional capacitors, relatively larger power densities and longer life cycles in comparison to batteries and traditional capacitors [9]. EDLC have electrodes that are fabricated from porous, high surface area carbon materials. The materials of construction for pseudocapacitors are transition metal oxides and/or conductive polymers [10]. A very important difference between EDLCs supercapacitors and conventional capacitors is that in EDLC supercapacitors there is no dielectric layer as in capacitors. Instead, both electrodes are immersed in an electrolyte solution and are separated by a very thin, semi-permeable insulator called a separator [10]. Traditional capacitors rely on the dielectric material to store the charge; that is why the capacitance of traditional capacitors is limited by the dielectric material thickness. ELDC supercapacitors operate by adsorbing/desorbing charged ions onto their highly porous, high surface area electrodes from an electrolyte [7]. When the plates are fully charged, an electric double layer is created because the opposite charge forms on either side of the separator. This is why supercapacitors are often referred to as double-layer capacitors or electric double-layer capacitors, EDLCs [7], but this is too restrictive, since there are many configurations that can potentially produce supercapacitors. Table 2.1 shows a comparison between the three types of energy storage devices: supercapacitor, battery, and capacitor.
Table 2.1: Comparison of main parameters of supercapacitors, batteries, and capacitors [11].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Supercapacitor</th>
<th>Battery</th>
<th>Capacitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge time</td>
<td>1-30 sec</td>
<td>0.3-3 hrs</td>
<td>$10^{-6}-10^{-3}$ sec</td>
</tr>
<tr>
<td>Discharge time</td>
<td>1-30 sec</td>
<td>1-5 hrs</td>
<td>$10^{-6}-10^{-3}$ sec</td>
</tr>
<tr>
<td>Energy density (Wh/kg)</td>
<td>1-10</td>
<td>20-100</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Power density (W/kg)</td>
<td>1000-2000</td>
<td>50-200</td>
<td>&gt;10 000</td>
</tr>
<tr>
<td>Cycle life</td>
<td>&gt;100 000</td>
<td>500-2000</td>
<td>&gt;500 000</td>
</tr>
<tr>
<td>Charge/discharge efficiency</td>
<td>0.9-0.95</td>
<td>0.7-0.85</td>
<td>≈1</td>
</tr>
</tbody>
</table>

The main difference between a supercapacitor and a capacitor is the specific power density and the specific energy density of each device. For capacitors having two parallel planer electrodes, separated by a dielectric material, the capacitance can be expressed as [2]:

\[ C = \frac{\varepsilon_r \varepsilon_0 A}{d} \quad \text{Eqn. 1} \]

\[ E = \frac{1}{2} (CV^2) \quad \text{Eqn. 2} \]

By substituting Eqn. 1 into 2:

\[ E_p = \text{Energy density} = (\frac{\varepsilon_0}{2}) \left( \frac{A}{d} \right) (\varepsilon_r \rho V_b^2) \quad \text{Eqn. 3} \]

Where \( C \) is capacitance in Farads, \( \varepsilon_0 \) is the dielectric constant of a vacuum, \( \varepsilon_r \) is the relative dielectric constant, which is defined as \( \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \), where \( \varepsilon \) is the dielectric constant of the material, \( A \) is the total surface area of the electrodes in \( m^2 \), and \( d \) is the distance between the two parallel plates in \( m \). \( E \) is the energy stored in joules and \( V \) is
voltage difference between the electrodes in volts. \( \rho \) is the electrode density, and \( V_B \) is the dielectric material breakdown voltage. Eqn. 1 demonstrates that the capacitance of the capacitor is strongly dependent on the plate’s area, distance between plates, and the dielectric material used. The capacitance can be increased by increasing the area of the electrodes, decreasing the distance between them, and using a dielectric material with high value of \( \varepsilon \) [2]. Since the widespread use of capacitors is limited by their low energy storage density, it is important to focus on the factors that might be changed to manipulate the energy density. Eqn. 3 demonstrates that the capacitor energy density can be maximized by changing the geometry of the capacitor and the properties of materials of construction. The double layer capacitance of a typical smooth electrode surface is about 10-20 \( \mu \text{F/cm}^2 \). This value can be increased to 100 F/g by increasing the electrode surface area and using conducting materials that have a specific surface area of 1000 \( \text{m}^2/\text{g} \) [12].

2.3 Multilayer Capacitors and Printing Technologies

There are numerous studies focusing on the development of new materials, new geometries, and new electrolytes for supercapacitors. An electrolyte is used in electrochemical capacitors. This research is not focusing on the use of electrolytic supercapacitors. Instead, multilayer capacitors were fabricated by stacking capacitors using conducting, high surface area nano-materials for the electrode layers, separated by dielectric layers. The aim is to print multilayer capacitors focusing on decreasing the thickness of the dielectric layer as much as possible and maximizing the electrode surface area by using different nanomaterials with high porosity.
The attraction of direct printing for the fabrication of flexible electronics devices including multilayer, stacked capacitors results from the possibility of creating stacks of thin-film devices in a low cost, simple, fast manufacturing process [13]. There are five major printing processes: flexography, screen, non-impact, gravure, and offset [14]. The printing method used is determined by the properties (chemistry, viscosity and surface tension) of the inks and by the printed products’ technical and economic considerations. Screen and inkjet printing methods are best for high accuracy, low volume production, while flexographic, gravure, and offset are used more commonly for high volume production [14]. Table 2.2 shows the differences in ink viscosity requirements and the dry film thicknesses for these common printing methods.

Table 2.2: Ink viscosity requirements and dry film thicknesses for common printing methods.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravure</td>
<td>30-200 cps @25 ºC</td>
<td>Up to ≈5.5 μm</td>
</tr>
<tr>
<td>Flexographic</td>
<td>50-500 cps @25 ºC</td>
<td>Up to ≈2.5 μm</td>
</tr>
<tr>
<td>Screen</td>
<td>1,000-50,000 cps @25 ºC</td>
<td>Depends on the mesh width, around 7-30 μm</td>
</tr>
<tr>
<td>Inkjet</td>
<td>Aqueous inkjet 1-3 cps @20 ºC</td>
<td>0.2-2 μm</td>
</tr>
<tr>
<td></td>
<td>Continuous inkjet 1-5 cps @20 ºC</td>
<td>0.2-2 μm</td>
</tr>
<tr>
<td></td>
<td>UV Curing ink 50-100 cps at ambient temp.</td>
<td>1-20 μm</td>
</tr>
</tbody>
</table>

2.4 Screen Printing

Screen printing is one of the five basic printing methods. The concept is to transfer a desired image by pushing a very viscous ink through openings in a stencil that has been
applied to a mesh stretched over a wooden or metal frame. A flexible squeegee is used to force or pump ink through the stencil openings to wet the substrate during the squeegee stroke [16]. In Table 2.2, it can be seen that for the screen printing process, the ink viscosity requirement is the highest among the other listed printing methods. Screen-printing, which was used in this project, can deposit thick ink films and fine lines, which are more durable than those applied by other printing methods [14].

In general, for the flat bed screen, the image carrier will consist of the frame, the woven screen, and the stencil. The screen frame holds the screen fabric without wrapping, is at least 4 inches wider and 4 inches longer than the largest stencil to be reproduced, and is deep enough to hold the ink to be printed without spilling [16]. One of the advantages to screen-printing is that there is no standard shape or size for a screen printing frame.

The woven screen fabric is attached to the frame under tension. There is no one fabric that can be used for all screen printing applications. When selecting the screen fabric, many things should be considered: the type of stencil and ink to be screened, the quality of the substrate that is to receive the ink, the fineness of image line detail desired, and the number of impressions [16]. The woven screen-printing fabric serves the functions of supporting the stencil and holding or metering the ink through the open areas. The basic concept of screen printing is based on the use of a stencil. A stencil can be made by sketching some outline and then cutting out the sketch. Stencils can be classified into three groups: hand-cut, tusche-and-glue, and photographic. Hand-cut stencils are made by manually removing the printing image areas from the base or support material. Tusche-and-glue stencils are produced by using a lithographic tusche, an oil-based pigment, to draw directly on the screen fabric and then blocking out non-image areas with a water
based glue material. Photographic stencils are generally produced using a thick, light-sensitive, gelatin-based emulsion that is exposed and developed either on supporting film or directly on the screen itself [16]. There are many characterizations or specifications of the mesh that affect the achievable ink film, such as [17]:

- **Mesh count**: Refers to the number of wires per linear inch. As the mesh count increases, the volume of ink deposited through the screen decreases. For example, a 105 mesh count would be 105 X 105, or 11,025 opening per square inch in a plain weave.

- **Mesh open area**: The percentage of total open space area in total screen area. It is dependent upon the wire diameter and the mesh count (See Figure 2.1).

- **Mesh thickness**: Theoretically, the overall mesh thickness is twice the wire diameter; however, it is rarely reached in practice. The actual overall thickness can be three times the wire diameter in extreme cases.

- **Mesh orientation**: The orientation of weft and warp wires to the frame. Mesh can be mounted at a 22.5°, 30°, 45°, or 90° orientations to the mesh weave of the frame.
2.5 Review of Materials Used in Supercapacitor Electrode Construction

Currently, various carbon materials are being used to print supercapacitor electrodes, due to their high conductivity, high surface area, favorable mechanical properties, relatively low cost, controlled pore structure, and ease of processing. The cost of carbon nanotubes, CNT, has been reduced significantly over the last 20 years [18]. The advantage of using CNT is in maximizing the overall gravimetric performance of the capacitor by increasing the electrode-electrolyte contact and decreasing the device weight because CNT electrode materials can be confined to a smaller area [10].

The capacitance typically ranges from 15-135 F/g for CNT and from 40-140 F/g for activated carbon [7]. The literature shows a very widely investigated method to enhance a capacitor’s performance: mixing or coating the carbon materials with active transition metal oxides, such as manganese oxides or with conducting polymers such as polyaniline.
and polypyrrole, and use of modified carbon materials as the electrode material [7]. For example, the mixing of activated carbon with a transition metal oxide increases the specific capacitance by a factor of 10-100, depending on the type of metal oxide used [20]. Also, polypyrrole coated CNTs can reach a capacitance of 170 F/g [7], while MnO$_2$ coated CNTs can attain a capacitance of 149 F/g [7].

Graphene-based supercapacitors have also been widely studied and have demonstrated a specific capacitance of a little over 1—F/g [7]. Graphene electrochemical properties can be enhanced by modifying the graphene. For instance, graphene can be modified by preventing single or a few layers of graphene sheets from agglomerating to obtain a higher effective surface area [7]. Wang et al. [21] demonstrated that by using a gas-solid reduction process to avoid graphene aggregation, a maximum specific capacitance of 205 F/g with an energy density of 28.5 Wh/kg could be achieved at 1V in an aqueous electrolyte, which is higher than CNT-based supercapacitors.

Markoulidis et al. [22] explored the performance improvement of an electrochemical supercapacitor based on activated carbon (AC)/multi-wall nanotubes (MWNTs)/polymer binder nano-composite electrodes. It was established that an AC-based supercapacitor with 0.15% w/w MWNT content and 30 μm roll-coated electrodes, with the cell immersed in the electrolyte, increases conductivity and enhances specific capacitance two to more than three fold in comparison to AC/polymer binder electrode-based capacitors. This significant increase in both capacitance and conductivity is due to the MWNT network lacing the AC particles surface and creation of more pores. AC has a large porosity, which reduces its conductivity; MWNTs are added to increase the conductivity.
Wu et al. [23] synthesized novel supercapacitors with a coaxial tubular morphology based on sodium alginate-multiwalled carbon nanotubes/polyaniline (SA-MWCNTs/PANI). The results show that the SA-MWCNTs/PANI nanocomposites achieved a specific capacitance of 442 F/g at 0.5 A/g current density.

Ranade et al. [24] optimized the composition and the thickness of a supercapacitor electrode based on active and conductive carbon and binder. First, electrodes were prepared with fixed thicknesses and different compositions. In order to get the optimum percentage of active-conductive carbon, the specific capacitance obtained for each electrode material used in the assembly of the capacitor was measured. The result suggested that capacitance was directly proportional to the amount of conductive carbon. The optimum level of capacitance was reached at 7% w/w of conductive carbon. The capacitance started to decrease as the conductive percentage was increased further. The electrode thickness then was optimized for electrodes of different compositions from 50-250 microns. The results showed that capacitance was directly proportional to thickness.

Ryan et al. [25] in their review paper mentioned that some groups that inkjet printed carbon nanotube sheets, were able to obtain a sheet resistivity below 1 kΩ/□, using multiple layers of CNT. The lowest achieved sheet resistance, as stated in the Ryan et al. review paper, was 78 Ω/□ with 200 printed layers. Taking the print layers into account, the lowest recorded sheet resistance was 760 Ω/□ with 12 prints.
2.6 Research Objectives

It is hypothesized that the addition of silver flake and silver nanowire inks into a CNT ink, used for printing the electrode layers of capacitor, will improve the device capacitance for two reasons: first, by lacing the tubes of CNT, thus creating more pores to store more electric charge, and, second, the conductivity of silver is very high, which will improve the conductivity of the CNT sheet conductivity. The aim of this study is to evaluate this hypothesis by:

- Determining the impact of adding a silver flake ink, or silver nanowire to a CNT ink’s conductivity after printing. Also, to determine the optimum percentage of silver and structure of silver to (nanowires or silver flake) added to CNT ink to improve its functional performance.

- Studying the influence of calendering the multi-layer capacitor electrodes on its conductivity and surface topography.

- Creating a complete multi-layer printed capacitor using the optimum formulated conductive ink blend as the electrode layer material by screen printing alternative layers of dielectric and the optimum conductive ink blend on top of each other on a polyethylene terephthalate (PET) substrate and comparing the capacitance of these devices created.

In addition, a graphite ink will be fabricated from a synthetic graphite powder and conductive carbon black powder, and its bulk conductivity will be compared with the commercial CNT ink used in this work.
CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials

A list of materials used in this study is shown in Table 3.1-a. More description of CNT ink, silver flake ink, and nanowires are shown in Table 3.1-b.

Table 3.1-a: List of materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Product No. or Description</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-Walled Carbon Nanotubes screen ink SWCNT</td>
<td>SG76-Ink-001</td>
<td>SWeNT, Norman, OK</td>
</tr>
<tr>
<td>silver flake, water-based screen ink</td>
<td>HPS-021LV (Water-based screen ink)</td>
<td>NovaCentrix, Austin, TX</td>
</tr>
<tr>
<td>Silver Nanowires</td>
<td>SLV-NW-90</td>
<td>Blue Nano, Charlotte, NC</td>
</tr>
<tr>
<td>Dielectric screen ink</td>
<td>Acheson Electrodag PF-455B</td>
<td>Henkel, Irvine, CA</td>
</tr>
<tr>
<td>Synthetic graphite powder</td>
<td>Nano25 (surface area 172.08 m²/g)</td>
<td>Asbury Carbon Co., Asbury, NJ</td>
</tr>
<tr>
<td>conductive carbon black powder</td>
<td>5303 (surface area 254 m²/g)</td>
<td>Asbury Carbon Co., Asbury, NJ</td>
</tr>
<tr>
<td>Acrylic resin solution</td>
<td>Joncryl HPD 296</td>
<td>BASF Corp., Wyandotte, MI</td>
</tr>
<tr>
<td>Film forming acrylic polymer emulsion</td>
<td>Joncryl 624</td>
<td>BASF Corp., Wyandotte, MI</td>
</tr>
<tr>
<td>Polyethylene terephthalate (PET) sheets</td>
<td>Melinex ST 506</td>
<td>DuPont, Chester, VA</td>
</tr>
</tbody>
</table>
Table 3.1-b: Description of commercial CNT ink, silver flake ink, and nanowires.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ingredients</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotube ink</td>
<td>- Water (0.5-15 wt%).</td>
<td>Diameter: 0.93 nm</td>
</tr>
<tr>
<td>(Single Wall Nanotubes)</td>
<td>- Co-solvent (Ethanol, 2-Butanol, 1-Pentanol, 1-Hexanol) (40-50% wt%).</td>
<td>Aspect Ratio: 1600</td>
</tr>
<tr>
<td></td>
<td>- Carbon as Single-Walled Nano Material (0.1 wt%).</td>
<td>Specific Surface Area: 790 $m^2/g$</td>
</tr>
<tr>
<td>Silver flake ink</td>
<td>- Ag flake (75 wt%).</td>
<td>Disk like</td>
</tr>
<tr>
<td>(NovaCentrix)</td>
<td>- Water (Main solvent).</td>
<td>Particle size: 2 microns</td>
</tr>
<tr>
<td></td>
<td>- Fraction of glycols, glycerin and PVP in the solvent (To promote stability of the flakes in solution)</td>
<td>Thickness: 50-200 nm</td>
</tr>
<tr>
<td>Silver Nanowires</td>
<td>- Silver (1.25 wt%).</td>
<td>Diameter: 90 nm</td>
</tr>
<tr>
<td>(Blue Nano)</td>
<td>- Ethanol (Solvent)</td>
<td>Length: 25 $\mu$m</td>
</tr>
<tr>
<td></td>
<td>- Polymer (&lt;0.5 wt%)</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Carbon Ink Formulation

3.2.1 Synthetic Graphite Powder (Nano25), Ink A

Ink A was formulated by adding 29.81 g synthetic graphite powder (Nano25) to 52.5 g of 5 wt.% ammonia in DI water under slow agitation. Once all the graphite powder was added to the ammonia DI water, the mixture was mixed for 5 min, and then the pH was checked since it should be adjusted between 8-9 if necessary with 5 wt.% ammonia in DI water. The pH of the mixture was found to be about 9. Next, 27.4 g solution resin (HPD296) was added to the mixture to disperse the graphite powder. After adding the solution resin, foaming was observed; so 5 g of ethanol was added. The mixture was then
mixed at low speed with a laboratory mixer for 45 min. 1.85 g of a film forming emulsion resin (Joncryl 624), was added to improve the ink’s printing and adhesion. After the ink was mixed for 15 min, it was printed with a Byrd bar. It showed good film adhesion to PET, but the sheet resistivity was high, 770 Ω/□.

3.2.2 Conductive Carbon Black Powder (5303), Ink B

To formulate Ink B, 7.55 g of 5 wt.% ammonia DI water and 20.95 g solution resin (HPD 269) were mixed in a laboratory mixer at low speed. 12.79 g of conductive carbon black powder (5303) was then added slowly to the mixture. The pH was checked continuously to make sure it was maintained at 7 or higher. 4.6 g ethanol was then added to prevent foaming and the ink was mixed at medium speed in a blender for two hours. After two hours, 9.79 g emulsion resin (Joncryl 624) was added and the ink mixed for an additional hour. Ink B had a high viscosity, and it showed very poor adhesion when it was printed using a Byrd bar.

3.2.3 Blending Ink A and B

The two non-functional inks, A and B, were mixed by weight at different percentages to obtain a third ink with better adhesion and conductivity properties. Three test samples were prepared: the first ink contained 47.8 wt.% ink A and 52.2 wt.% ink B. The second formulation contained 67.5 wt.% ink A and 32.5 wt.% ink B. The third ink contained 74 wt.% ink A and 26 wt.% ink B. Each blend was drawdown printed with a Byrd bar. The formulated ink with the best adhesion and highest conductivity was selected from the three blends and designated Ink C, and a large batch was prepared for additional studies.
3.3 Blending Silver with Commercial CNT Ink and Formulated Graphite Ink

In this phase of the work, graphite ink was blended with silver flake ink (NovaCentrix, Metalon HPS-021LV, Austin TX). Carbon nanotubes were blended with silver nanowires and silver flake ink, separately at different percentages. Inks were blended with silver to study the effect of silver addition on the sheet resistivity of a capacitor’s electrode layer and to determine the optimum percentage and shape of silver for minimizing the sheet resistivity of the CNT and graphite printed layers.

3.3.1 Graphite Ink Blending with NovaCentrix Silver Flake Ink

A Graphite ink was blended with NovaCentrix silver flake ink at seven silver percentages: 5, 10, 15, 20, 25, 30, and 35 wt.%, respectively. 6.69 g of graphite ink (25 wt.% graphite) was blended with 0.526 g of silver flake (75 wt.% silver) to prepare a blend of 20 wt.% silver flakes and 80 wt.% graphite, and so on to achieve the different wt.% ink blends.

3.3.2 CNT Ink Blending with NovaCentrix Silver Flake Ink and Silver Nanowires

Silver nanowires were blended with CNT ink at six different weight percentages: 2, 5, 8, 10, 20, and 30 wt.%, respectively. For example, a blend of 20 wt.% of silver nanowire in CNT was prepared by adding 2.22 ml silver nanowire to 1.11g CNT ink, and so on to create all the different weight percentages.

Blends of silver flake screen ink and CNT ink were prepared at different silver flake percentages: 5, 10, 20, 35, 50, 75, and 90 wt.%, respectively. A blend of 20 wt.% silver
flake and 80 wt.% CNT was prepared by manually mixing 50 g CNT ink with 5.36 μl silver flake ink.

### 3.3.3 Printing Blended Inks

According to the DOE shown in Figure 3-1, each blend was draw-down printed on PET and cured in an oven at 120 °C for 10 min. After drying in the oven, the samples printed with the blends of NovaCentrix silver flake ink and CNT ink were sintered using a NovaCentrix PlulseForge 1200 unit at 370 V, 1400 μs, and 1.5 OLF at 20 FPM. After sintering the printed films, the roughness (Sₐ) and thickness of each film was measured with a Bruker GT-K Interferometer microscope at different locations and the average thickness and roughnesses were measured. The sheet resistivities, with units of (Ω/□), for the films were measured using a Four-Point Collinear Probe, and the bulk resistivity (Ω.cm) of each sample calculated from the measured sheet resistivities and sample thicknesses. Also, the bulk conductivity (Siemens/cm) of each sample was calculated as bulk conductivity = 1/bulk resistivity. Figure 3.1 shows the DOE for draw-down printed samples. The samples were coded according to the following scheme: CNT is Carbon nanotube ink, CNT-SF is CNT and Silver flake blend, and CNT-SNW is CNT and Silver nanowire blend. The blends were printed at different weight percentages and the number of prints for each sample are designated in Figure 3.1.
3.4 Multi-Layer Capacitor Fabrication

Multi-layer capacitors were screen-printed using an AMI MSP-485 semi-automated screen printer in two Phases.

3.4.1 Phase I: Printing the Electrode Layers and Screen Selecting

To prepare the first layer of the capacitor, the electrode was first screen printed using the CNT ink to select the proper screen. The mesh count of the first screen used was 325SS with 0.0005" of emulsion, and 0.0011" wire diameter at 45° wire angle. Based on the thicknesses of the CNT films obtained, a second screen was designed to obtain an ink film thickness three times greater in thickness to increase the conductivity of the printed layer. The specifications of the second screen used were 105SS with 0.0015" of emulsion, and 0.003" wire diameter at 45° wire angle. The pattern for both screens used was a 5×5 cm solid square block. From section 3.3, the formulation with the highest conductivity and best electrode layer performance was selected for printing and comparison with the CNT screen printed films. According to the DOE shown in Figure 3.1, the formulation with the highest conductivity and best electrode layer performance was selected for printing and comparison with the CNT screen printed films.
3.2, the first layer, the electrode, was screen printed on PET substrate sheet using two different inks: 35 wt.% silver flake and 65 wt.% CNT blend, or 100 wt.% CNT ink. The screen was cleaned using IPA after printing. Figure 3.2 shows the DOE for electrode printing. Samples were coded by ink used, screen used, and replicate number.

![Diagram of DOE for printing the electrodes layer.](image)

**Figure 3.2: DOE for printing the electrodes layer.**

After printing, the samples were thermally dried at a fixed temperature. They were dried at 120 C° for 10 min in an oven, determined by the properties of the ink and substrate. After drying, the samples printed with 35 wt.% silver were sintered at 370 V, 1400 μs, and 1.5 OLF at 20 FPM. Sintering was considered complete when the layer resistance no longer decreased with additional exposure. After sintering or drying, the roughnesses (Sₐ) and thicknesses of the films were measured with a Bruker GT-K Interferometer microscope. The sheet resistivities of the films were measured using a Four-Point Collinear Probe.
3.4.2 Phase II: Printing Complete Multi-Layer Capacitors

Three replicates of each condition selected in Figure 3.2 were used in Phase II to create a complete multi-layer capacitor. A stack of 3 layers was printed as shown in Figure 3.3 to obtain the completed final device. A dielectric layer (ELECTRODAG PF-455B) was printed on top of the electrode layer for each sample and were then cured using a Fusion UV drier equipped with the D bulb. The samples were passed through the UV drier 2 times. The third layer was printed on top of the dielectric layer of each sample using the same ink as was used to print the first layer. The samples were cured at the same conditions used for the first layer. The capacitance of , the final devices with three layers was measured using an E4980A Precision LCR Meter (Agilent Technology).

![Figure 3.3: Complete multilayer printed capacitor (Three layer structure).](image)

3.5 Calendering

Two samples of printed CNT electrode layers were joined with the printed sides facing each other, and were then calendered using different nip pressures (10, 25, 30 psi). One pass through the calender was used to smooth the film surface and remove the peaks in
the sheet resulting from the ink wires. After calendering, the roughness, thickness, and sheet resistivity of the electrode layers were measured again. They were then compared to the values without calendering to study the influence of calendering on the electrode conductivity and its surface topography, and to evaluate the complete multilayer capacitor performance.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Effect of Silver Addition to Commercial CNT Ink

4.1.1 Silver Nanowires
The silver nanowires were suspended in ethanol. It was found to be compatible with the CNT ink at 10 wt.% silver nanowires. Beyond this percentage, the two inks were incompatible and the blend was clearly unprintable and unstable as shown in Fig. 4.1-b. this observation agrees with what is mentioned in the silver nanowire’s technical data sheet, that silver nanowires will spontaneously aggregate when added to aqueous solutions with a low amount of ions [26]. The commercial CNT ink that was blended with the silver nanowires contained 0.5-15 wt.% water, which might be the reason for the incompatibility of the CNT and the silver nanowires at percentages beyond 10 wt.%.

Figure 4.1: Compatibility of CNT with silver nanowires.

a- CNT blended with 5% silver nanowires ink
b- CNT blended with 20% silver nanowires ink
Fig. 4.2 shows that adding silver nanowires to CNT ink decreased the sheet resistivity and increased the conductivity of the printed sheets. As mentioned in Table 4.1, addition of 2 wt.% silver nanowires to CNT decreased the sheet resistivity by ≈ 88%, and the bulk resistivity by ≈ 98%. Table 4.1 includes values of sheet and bulk resistivity for each blend. It also shows the percentage by which the sheet and the bulk resistivity decreased, when compared to CNT printed samples. Taking into consideration the cost and conductivity improvement, the optimum percentage of silver nanowires was found to be 3 wt.%. The decrease in CNT ink sheet and bulk resistivity is due to the high electrical conductivity of silver. Also, as stated in the Ryan et al. [25] review paper, when CNT ink is printed onto a substrate, a random network of CNT is left behind after the solvent evaporates. Some of the carbon nanotubes might be completely isolated and have no contact with any other carbon nanotubes. In that instance, electrons are constrained to a single carbon nanotube, which do not contribute to the conductivity of the printed sheet. Some of the CNT may be in contact with other CNT; this contact creates an electron pathway, ultimately resulting in electrical current, which is the reason for conductivity of printed sheets. So, mixing carbon nanotubes with silver nanowires, which has a high aspect ratio (= 277.78), might decrease the resistivity due to connecting the isolated CNT and forming long-range connectivity in the random systems, according to percolation theory.
Figure 4.2: The effect of silver nanowire addition to CNT ink on sheet resistivity.

Table 4.1: Values of sheet and bulk resistivity for samples printed using CNT and silver nanowires blends.

<table>
<thead>
<tr>
<th>Silver Nanowire wt.%</th>
<th>Sheet Resistivity, Ω/□</th>
<th>% of Sheet Resistivity Change</th>
<th>Bulk Resistivity, Ω.cm</th>
<th>% of Bulk Resistivity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (control)</td>
<td>153.60 (±0.87)</td>
<td></td>
<td>2.13E-03 (±5.13E-04)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>18.13 (±1.28)</td>
<td>-88.2 (±0.8)</td>
<td>3.8E-05 (±2.4E-06)</td>
<td>-98.2 (±0.3)</td>
</tr>
<tr>
<td>5</td>
<td>4.76 (±0.32)</td>
<td>-96.9 (±0.2)</td>
<td>1.2E-05 (±5.0E-07)</td>
<td>-99.4 (±0.1)</td>
</tr>
<tr>
<td>8</td>
<td>1.36 (±0.00)</td>
<td>-99.100 (±0.005)</td>
<td>2.5E-05 (±1.3E-05)</td>
<td>-98.8 (±0.3)</td>
</tr>
<tr>
<td>10</td>
<td>1.26 (±0.14)</td>
<td>-99.20 (±0.09)</td>
<td>1.0E-04 (±2.9E-05)</td>
<td>-95.2 (±0.2)</td>
</tr>
</tbody>
</table>

4.1.2 Silver Flake Water-Based Ink

The CNT ink was found to be compatible with the silver flake water-based ink at all percentages; no aggregation was observed. Samples that were sintered after curing in the oven had a sheet resistivity 28% less than samples cured in the oven alone. The influence
of different silver flake concentrations on sheet and bulk resistivity are shown in Fig. 4.3 and 4.4, respectively. The values of sheet and bulk resistivity of the printed blends are provided in Table 4.2 and the percentage by which addition of silver increases or decreases these values are in comparison to the control sample, CNT, are shown. It can be seen in Fig. 4.3 that the sheet resistivity decreased as the amount of silver flake increased in over the range of 0-10 wt.%. Beyond this weight percentage, silver addition increased sheet resistivity by 0.328% from the control sample to reach the maximum value of 154.1 \( \Omega/\square \) at 20 wt.% silver flake. The sheet resistivity decreased with the amount of silver flake addition. The average sheet resistivity of the samples printed using 35 wt.% silver flake is 87.29% lower than the average sheet resistivity of the control samples. Beyond 50 wt.% silver flake, addition of more silver is not useful because the percentage by which the resistivity is improved is almost the same. Based on the obtained data, if the selection of optimum silver concentration is based on sheet resistivity, the optimum silver flake percentage is 35 wt.%.

As shown in Fig. 4.4, bulk resistivity increased instead of decreased until it reaches the maximum value, 0.0156 \( \Omega \cdot \text{cm} \), at 10 wt.% silver flake. Beyond this point, the bulk resistivity continually decreased. The improvement of bulk conductivity started at a silver percentage of about 35 wt.%, where it measured 22.8% lower than the bulk resistivity of CNT ink printed samples. 75 wt.% silver flake ink needed to be added to CNT ink to decrease the bulk resistivity to about 98%, which can be achieved by adding 2 wt.% silver nanowires. Taking cost and bulk resistivity results into consideration, adding silver flake is not beneficial since it increases the bulk resistivity instead of
decreasing it. The reason for this might be that the silver flake is micro-sized which might separate and insulate the CNT instead of connecting them at these levels. At some point the resistivity starts to decrease and that might have nothing to do with percolation or connecting the CNTs. Silver flake at 35 wt.% might begin to dominate the resistivity response and the CNT began to act like an impurity, so the decreased resistivity is due to the high conductivity of silver.

Figure 4.3: The effect of silver flakes ink addition to CNT ink on sheet resistivity.

Figure 4.4: The effect of silver flakes ink addition to CNT ink on bulk resistivity.
Table 4.2: Values of sheet and bulk resistivity for each point in Figs. 4.3 and 4.4.

<table>
<thead>
<tr>
<th>Silver Flakes wt.% in the blend</th>
<th>Sheet Resistivity, $\Omega/\square$</th>
<th>% of Sheet Resistivity Change</th>
<th>Bulk Resistivity, $\Omega.cm$</th>
<th>% of Bulk Resistivity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (control)</td>
<td>153.60 ($\pm$0.87)</td>
<td></td>
<td>2.1E-03 ($\pm$5.1E-04)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>142.02 ($\pm$6.92)</td>
<td>- 7.5 ($\pm$4.0)</td>
<td>1.6E-03 ($\pm$3.76E-03)</td>
<td>+ 632.6 ($\pm$0.1)</td>
</tr>
<tr>
<td>10</td>
<td>115.58 ($\pm$9.62)</td>
<td>- 24.8 ($\pm$5.9)</td>
<td>9.8E-04 ($\pm$0.0)</td>
<td>+ 359.1 ($\pm$110.6)</td>
</tr>
<tr>
<td>20</td>
<td>154.10 ($\pm$6.41)</td>
<td>+ 0.3 ($\pm$3.6)</td>
<td>7.2E-04 ($\pm$2.5E-03)</td>
<td>+ 236.9 ($\pm$37.6)</td>
</tr>
<tr>
<td>35</td>
<td>19.52 ($\pm$2.73)</td>
<td>- 87.3 ($\pm$1.7)</td>
<td>1.7E-04 ($\pm$9.9E-04)</td>
<td>- 22.8 ($\pm$27.8)</td>
</tr>
<tr>
<td>50</td>
<td>0.82 ($\pm$0.13)</td>
<td>- 99.5 ($\pm$0.1)</td>
<td>1.3E-05 ($\pm$1.5E-05)</td>
<td>- 93.7 ($\pm$0.4)</td>
</tr>
<tr>
<td>75</td>
<td>0.13 ($\pm$0.01)</td>
<td>- 99.90 ($\pm$0.01)</td>
<td>3.8E-05 ($\pm$0.00)</td>
<td>- 98.2 ($\pm$0.5)</td>
</tr>
<tr>
<td>90</td>
<td>0.05 ($\pm$0.03)</td>
<td>- 99.96 ($\pm$0.02)</td>
<td>1.3E-05 ($\pm$0.00)</td>
<td>- 99.4 ($\pm$0.0)</td>
</tr>
<tr>
<td>100</td>
<td>0.032 ($\pm$0.008)</td>
<td>- 99.98 ($\pm$0.01)</td>
<td>3.4E-06 ($\pm$0.00)</td>
<td>- 99.8 ($\pm$0.0)</td>
</tr>
</tbody>
</table>

4.2 Multi-Layer Capacitor Fabrication

The average thickness of the CNT electrodes screen printed using screen with mesh count 325SS was 0.035 micron. The average roughness is 0.0154 micron, and the average sheet resistivity is $\approx 766 \, \Omega/\square$. Since the thickness was low, another screen with a mesh count 105SS was designed to deliver about three times more ink per print. The average thickness of CNT films printed using this screen was 155 nm. The average roughness was 0.0327 microns, and the average sheet resistivity for these films was $\approx 148.44 \, \Omega/\square$. Fig 4.5 shows the comparison between thickness and roughness for films printed using screen 1, and screen 2. Fig. 4.6 compares the sheet resistivity of the films printed using both screens.
4.2.1 Effect of Calendering on Sheet Thickness and Resistivity

Theoretically, it was expected that calendering the electrode layers using different pressure values would smooth the film surface, and eliminate the peaks resulting from the protruding CNTs as shown in Fig. 4.7. Since the dielectric layer needs to completely cover the electrode to prevent shorting between the two electrodes, calendering was
performed in an effort to flatten protruding CNTs. A thicker dielectric layer leads to a decrease in the complete device capacity since the distance between the capacitor electrodes is inversely proportional to the capacitor capacitance. The smoother the electrode layer is, the thinner the dielectric layer needed for coverage and the higher the capacitance of the device. After calendering, roughness, thickness, and sheet resistivity of the electrodes layers were measured again and compared to the values without calendering to study the influence of calendering on the electrode conductivity and its surface topography and, ultimately, on the complete multilayer capacitor performance.

Figure 4.7: Expected influence of calendering on the electrode layer surface topography and the dielectric layer thickness requirement.
As shown in Fig. 4.8, calendering had no influence on electrodes thickness, roughness, and sheet resistivity. Calendering had no effect on high CNT peaks, but it was found that it eliminated the short peaks.

![Before Calendering](image1.png) ![After Calendering](image2.png)

**Figure 4.8: Influence of calendering on surface topography of screen printed CNT film.**

**4.2.2 Ink Formulation Results**

Ink A, which was formulated using syntactic graphite powder (Nano25) as the pigment, showed good film adhesion when it was printed on PET, but the sheet resistivity was high, 770 \( \Omega/\square \). Ink B, formulated using conductive carbon black powder (5303) as the pigment, was thick and viscous, and it showed very poor adhesion when it was drawdown printed; these films readily peeled off the PET substrate after curing.

The two non-functional inks, A and B, were mixed manually by weight at different percentages to obtain an ink with better adhesion and conductivity properties. Three samples were prepared by mixing different portions of ink A and B to determine if a third better ink could be achieved. According to Table 4.3, films printed using a mixture of
67.5 wt.% ink A and 32.5 wt.% ink B, designated Ink C, achieved the best adhesion and highest conductivity.

Table 4.3: Sheet resistivity for sheets printed using different percentages of Ink A and B blends.

<table>
<thead>
<tr>
<th>Wt. % Ink A</th>
<th>Wt. % Ink B</th>
<th>Sheet Resistivity, Ω/□</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.8</td>
<td>52.2</td>
<td>117.8</td>
</tr>
<tr>
<td>67.5</td>
<td>32.5</td>
<td>104.2</td>
</tr>
<tr>
<td>74.0</td>
<td>26.0</td>
<td>167.7</td>
</tr>
</tbody>
</table>

Tables 4.4 and 4.5 include specifications of Inks A and B and Ink C, respectively. As shown in Tables 4.3, 4.4, and 4.5, adding 32.50% of Ink B to Ink A improves the sheet resistivity by 86.4%. This occurs even though adding ink B to ink A increases the emulsion resin wt.%, which increases sheet resistivity. This improvement might be related to the surface area of conductive carbon black, which was used to fabricate Ink B, which is ≈ 32.3% higher than the surface area of graphite powder, which was used to fabricate Ink A.

Table 4.4: Ink specifications.

<table>
<thead>
<tr>
<th></th>
<th>Ink A</th>
<th>Ink B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical carbon wt.% in wet ink</td>
<td>25.6</td>
<td>23.0</td>
</tr>
<tr>
<td>Theoretical solid wt.% in wet ink</td>
<td>34.8</td>
<td>45.2</td>
</tr>
<tr>
<td>Theoretical wt.% of carbon in solid</td>
<td>73.4</td>
<td>50.8</td>
</tr>
<tr>
<td>theoretical solution resin wt.% in wet ink</td>
<td>23.5</td>
<td>37.6</td>
</tr>
<tr>
<td>theoretical emulsion resin wt.% in wet ink</td>
<td>1.59</td>
<td>17.58</td>
</tr>
</tbody>
</table>
Table 4.5: Ink C specifications.

<table>
<thead>
<tr>
<th>Ink A and B amount composition</th>
<th>Ink A 67.50 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ink B 32.50 wt.%</td>
</tr>
<tr>
<td>Theoretical total carbon wt.% in wet ink</td>
<td>25.10%</td>
</tr>
<tr>
<td>Experimental total carbon wt.% in wet ink</td>
<td>23.62%</td>
</tr>
<tr>
<td>Theoretical graphite wt.% in wet ink (SA = 172.08 $m^2/g$)</td>
<td>20.80%</td>
</tr>
<tr>
<td>Theoretical conductive carbon black wt.% in wet ink (254 $m^2/g$)</td>
<td>4.30%</td>
</tr>
<tr>
<td>Theoretical emulsion resin wt.% in wet ink</td>
<td>4.58%</td>
</tr>
<tr>
<td>Theoretical solution resin wt.% in wet ink</td>
<td>26.10%</td>
</tr>
<tr>
<td>Theoretical solids wt.% in wet ink</td>
<td>36.77%</td>
</tr>
<tr>
<td>Experimental solids wt.% in wet ink</td>
<td>34.62%</td>
</tr>
<tr>
<td>Theoretical wt.% of carbon in solids</td>
<td>68.23%</td>
</tr>
</tbody>
</table>

4.2.3 Effect of Silver Flake Addition on Fabricated Graphite Ink

Graphite ink is compatible with silver flake water-based ink at all percentages; no aggregation was observed. Similar to section 4.1.2, sheet and bulk resistivity were investigated as a function of silver flake concentration and the results are shown in Figs. 4.9 and 4.10, respectively. Table 4.6 shows the percentage by which addition of silver decreases the sheet and bulk resistivity of each printed blend from the control sample, 100% graphite printed ink.
It can be seen in Fig. 4.9 and Table 4.6 that sheet resistivity decreases as silver flake content increases. Adding 5 wt.% silver flake reduced the sheet resistivity to 50.69%, compared to the 100% graphite ink. Based on the obtained data, if the selection of optimum silver concentration is based on sheet resistivity, the optimum silver flake content is 5 wt.% taking into consideration both the cost and conductivity improvement.

Bulk resistivity decreased with silver flake addition, but between 20 and 25 wt.% silver flake it increased. Beyond 25 wt.% silver flake level of addition, the bulk resistivity decreased. This might have nothing to do with connecting graphite; it is possible that the silver flake is dominating the properties, and graphite acting like an impurity. As a result, the decrease in resistivity might be due to the high conductivity of silver rather than an increase in the percolation.

![Graph showing sheet resistivity vs. silver flake wt% in ink](image)

Figure 4.9: The effect of silver flake ink addition to fabricated graphite ink on sheet resistivity.
Figure 4.10: The effect of silver flake ink addition to fabricated graphite ink on bulk resistivity.

Table 4.6: Sheet and bulk resistivity change for silver flake ink addition to Ink C.

<table>
<thead>
<tr>
<th>Silver Flakes wt.% in the blend</th>
<th>% of Sheet Resistivity Change</th>
<th>% of Bulk Resistivity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (control)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-50.69 (±0.731)</td>
<td>-11.93 (±6.992)</td>
</tr>
<tr>
<td>10</td>
<td>-50.69 (±4.627)</td>
<td>-16.10 (±19.333)</td>
</tr>
<tr>
<td>15</td>
<td>-55.32 (±4.222)</td>
<td>-31.12 (±11.737)</td>
</tr>
<tr>
<td>20</td>
<td>-56.22 (±4.141)</td>
<td>-29.87 (±13.835)</td>
</tr>
<tr>
<td>25</td>
<td>-58.10 (±3.979)</td>
<td>-27.35 (±10.249)</td>
</tr>
<tr>
<td>30</td>
<td>-70.50 (±2.887)</td>
<td>-54.75 (±5.253)</td>
</tr>
<tr>
<td>35</td>
<td>-63.13 (+/-1.080)</td>
<td>-62.77 (+/-7.229)</td>
</tr>
</tbody>
</table>
4.2.4 Multi-Layer Capacitor

After the capacitors were fabricated, the capacitance for each capacitor was calculated. Figure 4.11 shows the capacitance for the devices fabricated using CNT ink and a 35 wt.% silver flake and 65 wt.% CNT blend used for the electrode layers. As shown in Fig. 4.11, capacitors fabricated using silver flake and CNT blend as the electrode layers, have an 8.6% higher capacitance than CNT electrode based capacitors. As mentioned in Tables 4.1 and 4.2, sheet resistivity for a blend of 2 wt.% silver nanowires blended with CNT is almost equal to the sheet resistivity of the 35 wt.% silver flake blended with CNT. For this reason, a 35 wt.% silver flake and CNT was used to fabricate the electrode layers of the capacitors. The results seem to indicate that the addition of 2 wt.% silver nanowires to the CNT ink increased the capacitance by 8.6% in comparison to CNT electrode based capacitors. The optimum silver percentage and structure was found to be 3 wt.% silver nanowires blended with CNT ink. This combination resulted in a sheet resistivity ≈ 5 Ω/□, which is 72.4% higher than the sheet resistivity of electrodes prepared from the 35 wt.% silver flake, and the 65 wt.% CNT ink. The calculated relative permittivity for the dielectric material used to separate the electrodes layers was determined to be 2.87, for a dielectric layer thickness of 21.66 micron. In figure 4.11 the CNT ink printed using screen 1 had a film thickness of 0.03 microns, the same as CNT ink printed with screen 2 had a film thickness of 0.16 microns, and the CNT-SF ink had a film thickness of 0.8 microns.
4.3 Conclusions

It was found that the addition of 2 wt. % silver nanowires to CNT ink decreased the sheet resistivity of printed CNT electrodes by 96.8%. Taking cost and resistivity results into consideration, adding silver flake to CNT is not of benefit. The reason for this might be that the silver flake is micro-sized, which might separate and insulate the CNT instead of connecting them. Calendering was found to have no influence on electrode thickness, roughness, or sheet resistivity. However, it was found that calendering eliminated the presence of short peaks. Capacitors fabricated using a 35 wt. % silver flake and 65 wt. % CNT blend for printing the electrode layers enabled an 8.6 % increase in capacitance over CNT electrode-based capacitors. The optimum silver percentage and structure was found to be 3 wt. % silver nanowires blended with CNT ink. This formulation provided the optimum sheet resistivity of ≈ 5 Ω/□, which was 72.4% higher than the sheet resistivity of electrodes printed with the 35 wt. % silver flake and 65 wt.% CNT. If those optimum
ink conditions were used for printing capacitor electrodes, the capacitance would be much more than 8.6% higher than the capacitance of CNT electrode-based capacitors. The relative permittivity for the dielectric material printed between electrodes layers was calculated to be 2.87. Ink was formulated from graphite powder, and the printed sheet resistivity reached 327.8 Ω/□ with a bulk resistivity of 0.432 Ω.cm. Commercial CNT ink has a sheet resistivity equal to 153.6 Ω/□ and a bulk resistivity equal to 0.002 Ω.cm. To compare the two inks, CNT has a sheet resistivity about 53% lower than formulated ink, and bulk resistivity twice that of the formulated ink. The CNT ink is more conductive, but it is more expensive than the Ink C formulation. Ink C sheet resistivity was reduced 50.7% by adding 5 wt.% silver flake, and its bulk resistivity was decreased 12% by adding 5 wt. % silver flake.

4.4 Recommendations for Future Studies

In order to get more sheet conductivity improvement, it is recommended that a nano-particle silver ink be mixed with the CNT ink instead of using larger micro-sized silver flake particles. It is also recommended to fabricate an ink from "scratch" using CNT and silver nanowire powders to avoid any aggregation and incompatibility issues. In addition, it is recommended to print a stacked capacitor with more than three layers to increase overall capacitance. Finally, the squeegee speed and lift off height affect the printed film roughness, so it is recommended to use different squeegee speeds and lift off heights in future studies. The squeegee forward and return speed used at this research were 2.41 inch/sec and 1.62 inch/sec, respectively.
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