Capacitors Out of Recycled Printed Electronics Paper Substrates

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Abstract

The purpose of this project was to investigate the possibility of recycling conductive ink printed paper substrate previously used in printed electronics, and reworking it into a conductive paper. Such conductive substrate was further used as a conductive layer in capacitor construction. Firstly, paper printed with conductive carbonaceous ink was re-pulped. Substrate was torn into small pieces 2”x2”. The goal of re-pulping was to make suspension of ink and paper fibers.

Secondly, paper handsheets were prepared with additional amounts of conductive material. The electrical conductivity of the prepared handsheet was determined and electrical properties recorded. Further, a dielectric solvent-based ink was formulated using vacuum metalized flake aluminum pigment (VMP) and vinyl based resin. Vacuum metallized flake provides smooth metallic finish. Flake itself was not covered with fatty acid as found on traditionally milled aluminum flakes. Dielectric ink formed larger area then conductive graphite ink that was deposited on the top of dielectric layer. Conductive ink was prepared using graphite with the Brunauer–Emmett–Teller (BET) surface area of >500 m2/g respectively. Graphite chosen for this experimental work has platelet morphology. The diameter of the selected platelets was 15-25 microns. The thickness of the platelets was in the range of 10-15 nm. Ink was prepared using water-based formula. Binder for the ink was a commercially available acrylic based resin suitable for direct and indirect food contact applications. The prepared inks were applied onto the conductive paper substrate. Sheet resistance of conductive layers was measured via 4-point probe method. First down was dielectric aluminum based ink. Air-drying after printing was done in hot air oven at 120˚C for 5 minutes. Functionality of prepared capacitor

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was tested via Precision LCR meter (Agilent E4980A). It was demonstrated that it is possible to reuse graphite printed substrates formerly used in printed electronics for building new conductive structures such as a capacitors.

Introduction

Due to growth of printed electronics market, conductive inks market for printed electronics (PE) is rapidly expanding. Conductive inks will constitute $3.36 billion market in 2018. According to IDTechEx, it is forecasted that silver and copper inks will represent $735 million market only [1]. With increased production and use of these metal-based PE inks, increased post-consumer waste and waste from production will increase as well.

Capacitors can be charged using different ways and can be manufactured using various electrodes types [2]. Frequently, graphene and graphite could serve as supercapacitor in high-power applications, or printing circuits, sensors, antennae, touch screens, display panels, and thermally conductive print applications. This would be due to their unique morphology, high surface area (1 to > 2000m^2/g) and electrical characteristics [2]. Carbonaceous materials can be used to fabricate negative and positive electrodes. Graphite pigments can have various morphologies; therefore graphite-based inks have numerous properties and can be classified into four categories, a) conductive, b) semiconductive, c) dielectric, and d) resistive inks. The application areas for these functional inks have been expanding rapidly in the recent years, including touch screens, printed circuit boards, display panels, RFID (Radio Frequency Identification) tags, and sensors [3-5].

Graphene, which is a single sheet of graphite, is actually a semiconductor due to linear dispersion structure of π-π^* orbital, which leads to overlapping between the valence and conductance bands, forming a semiconductor. This material has very high carrier mobility (200,000 cm2/V·s), optical transmittance (98%), stiffness (1TPa), and thermal conductivity (5000 W/mK), yet the resistivity is limited (50-6500 Ohm/sq), [6]. Graphite, which has multi-layer structure of graphene sheets, is a conductor due to parabolic dispersion structure of π-π^* orbital, which creates overlap between valence and conductance bands, forming semi-metal conductor. The resistivity of these graphite materials is in the range of 10^{-3}-10^{-4} Ohm/sq. Generally, one to two layers of graphene sheets (with thickness less than 1nm) are considered semiconductor while 3 or more layers of sheets (thickness more than 1nm) are considered conductor [6]. Graphene inks would have a high potential if sufficient levels of conductivity could be achieved. This would open many applications in the field of printed electronics. Such applications range from the printing of circuits and antennae, or supercapacitors [7] to the production of coated films for EMI (electromagnetic interference) shielding, or touch screen devices [8]. There is tremendous potential for modification and/or improvement of electrical properties of graphene, and the estimates for potential market size range into the billions of dollars annually. Graphene nanosheets can be efficiently used alone, or as nanocomposites with different materials for modified electrical properties [9], in combination with Ag [10], or carbon nanotubes [11, 7] or PEDOT: PSS [12,13] for improved conductivity. Graphene nanoplatelets can be anionically modified in order to enhance conductivity of fully printed batteries [14]. Conductive inks based on graphene nanoplatelets are significantly less expensive than inks with metallic fillers such as silver, gold, or silver coated copper.

Electronic circuits consist of active and passive elements, of which capacitors, resistors and inductors belong to passive structures, representing about 80% of circuit boards. Among the passive components, the capacitors are the predominant circuit board structures, used in electric field to store the energy. Basic structure of capacitors involves two layers of conductive material separated by a thin layer of insulating film. The thickness and quality of these layers is critical to the performance of the final capacitor. Separator or dielectric layer is ion permeable but electrons blocking membrane. Its role is to avoid short circuits between the electrodes. In addition, the dielectric layer is responsible for increased capacitance by reducing the strength of the electric field. Capacitors are formed by the stacking dielectric materials between two conducting plates. Their capacitance is defined as

$$C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot A}{d} \tag{1}$$

Where A is the area, d the distance between plates, ε0 the permittivity of free space, and εr is the relative permittivity of the dielectric material. $\varepsilon_0\varepsilon_r = \varepsilon$ is permittivity of the material. To achieve very high capacitor performance, a combination of maximizing the plate area, minimizing the distance between plates and selecting a dielectric material to maximize the effective permittivity can be used. The permittivity is based on the properties of the dielectric material, whether deposited/printed, or the original substrate itself. The area can be effectively manipulated using a number of geometric techniques; such as stacking alternating plates or rolling up a flat capacitor. The aim of this work is to construct capacitor from recycled conductive carbon material filled with cellulose fibers.

Experimental procedure

The first part of the experimental work was focused on re-pulping, handsheet preparation and evaluation of graphite based handsheet formation. Second part of the experiment was aimed towards preparation of dielectric and conductive inks along with capacitor constructing. A MicroMaelstromTM Laboratory Pulper (Figure 1) was used for substrate pulping. Duration of pulping was set up to 8 minutes at 600 RPM. Parameters for paper recycling are listed in Table1.

Figure 1: *MicroMaelstrom™ laboratory pulper*

Consistency of the repulped stock was calculated and was subjected to preparation of the electrically conductive handsheets. Additional amounts of graphite were added into paper slurry with objective to improve its electrical properties. With additional amounts of graphite, the formation of the handsheets was monitored.

Consistency of Paper Fibers [%]	6
Water Temperature [˚C]	25
Re-pulping Time [min]	8
Pulper Speed [RPM]	600

Table 1: *Paper Dispersion*

Further, electrically conductive and insulating inks were formulated. Dielectric ink was solvent based while conductive ink based on graphite flakes was water-based.

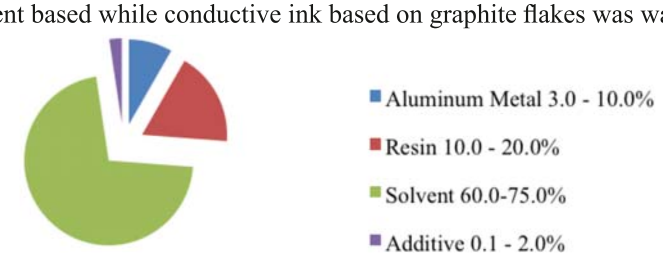

Figure 2: *Composition of solvent based dielectric ink*

The conductive ink formulation was done using commercial styrene-acrylic resin. The representation of the ink formulation is depicted in the Figure 3.

Figure 3: *Composition of water based conductive ink*

The capacitance measurements were done with Agilent E4980A Precision LCR meter. Electrical properties of conductive paper substrate and printed inks were tested using a Kethley 2000 multimeter and 4-probe technique.

Figure 4: *Agilent E4980A Precision LCR meter*

Results and discussion

Paper substrates printed with conductive inks were repulped and newly formed paper handsheets were prepared. The original print did not provide enough of conductive material to satisfy the conductivity requirements for the first layer of the capacitor. The formed paper was therefore doped with additional levels of graphite flakes. Ratio of the graphite to paper fibers was monitored.

Figure 5: *Base handsheet prepared from recycled carbon printed substrate*

Some of the benefits of the handsheets over graphite printed on PET (graphite dispersion without binder) are that there is no graphite smudging. In addition handsheets withstand the bending and are not brittle. Therefore further calandering can follow.

Figure 6: *Conductive papers with different graphite loading*

	Ratio of Graphite to Paper Fiber						
Graphite "15"	100	95	75	65	55	45	40
Paper Fiber	0	5	25	35	45	55	60
Handsheet Formation	Uniform Not possible to detach from wire	Uniform Not possible to detach from wire	Uniform Not possible to detach from wire	Uniform Not possible to detach from wire	Uniform Partially possible to detach from wire	Uniform, Partially detachable from wire	Uniform, **possible** to detach from wire

Table 2: *Composition of graphitic handsheet using 15 micron graphite grade*

	Ratio of Graphite to Paper Fiber						
Graphite "25"	100	95	75	65	55	45	40
Paper Fiber	0	5	25	35	45	55	60
Handsheet Formation	Uniform Not possible to detach from wire	Uniform Not possible to detach from wire	Uniform Not possible to detach from wire	Uniform Not possible to detach from wire	Uniform Partially possible to detach from wire	Uniform, Partially detachable from wire	Uniform, **possible** to detach from wire

Table 3: *Composition of graphitic handsheet using 25 micron graphite grade*

Figure 7: *Formation of the graphite paper using TAPPI handsheet mold*

The ultimate goal of this experimental work was to create two layers conductive and insulating layer in one manufacturing step. In order to prepare the second-dielectric layer of the capacitor, selected area was kept open while the conductive base sheet was covered with masking sheet.

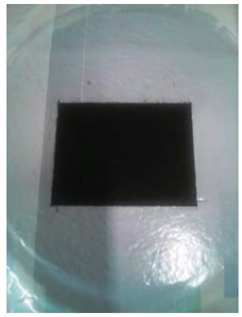

Figure 8: *Masking sheet covering conductive layer and accepting dielectric material*

Graphite Grade	Sheet Resistivity [Ohms/sq]
15micron Grade	5
25micron Grade	8

Table 4: *Sheet (surface) resistivity of "graphite handsheets"*

Sample ID Based on 15 µm grade	Fibers: Pigment	Thickness [mils]	Sheet Resistivity [Ohms/sq]	Sheet Resistance [Ohms/sq]*mil
A	1.5:1 (60%: 40%)	35.1	7.6	1232
B	3:1 (75%: 25%)	18.92	9.7	843
C	1.5:1 (60%: 40%)	17.5	28.7	2309
D	3:1 (75%: 25%)	10.8	36.77	1822

Table 5: *Conductive paper properties*

Larger scale graphite (25 micron) resulted in somewhat inferior electrical properties than smaller graphite particles (15micron), as shown in the Table 4. Therefore, smaller grade was chosen for further evaluation and paper formation.

Further, the study focused on the relationship between paper fibers amount and quantities of the graphite material (Table 5). Sample A and C were compared as well as B and D due to same composition but different thickness of the final sheet. It was observed that not only fiber to pigment ratio plays role in the final electrical properties but also thickness of the sheet influences conductivity (Table 5). It is believed that thickness of the sheet represents "taller" stack of the conductive material and so the flow of the electrons within the paper is more efficient.

It was expected that sheets with higher pigment loading (A and C) would result in superior electrical properties as those that were composed with more paper fibers. In contrary, sheets with 75% paper content (sheet B) resulted in somewhat better conductive sheets. It is probable that the larger fiber network allows better paper formation and thus more efficient graphite support and alignment.

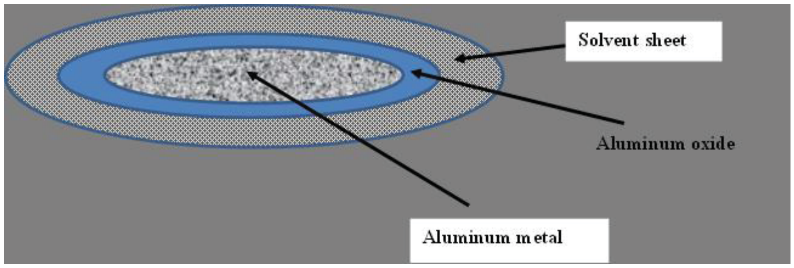

Figure 9: *Aluminum flake*

Figure 9 illustrates anatomy of aluminum pigment. Aluminum metal is covered with insulating layer of aluminum oxide. The aluminum flakes form ink layer in very smooth mirror like way, which is very convenient and necessary for ideal dielectric layer.

Layer	Sheet Resistivity [Ohm/sq]	Thickness [microns]
Conductive Base Sheet	55	15
Conductive Carbonaceous Ink	35	8

Table 6: *Electrical properties of capacitor substrate layers*

Table 6 indicates that the conductive base sheet was less conductive than the graphite ink alone, which was expected. Cellulose fibers along with recycled graphite created solid conductive network, which increased in conductivity after blending in fresh graphite.

Capacitor	Capacitance [Farad]
A	3.2e-10

Table 7: *Capacitance measurement of final parallel plate capacitor*

Capacitors were constructed based on recycled graphite sheets filled with fresh graphite, insulating layer made of aluminum ink and conductive layer made of graphite ink layer. The capacitance of the printed capacitors was 320 pF at 1000 Hz (Table 7).

Conclusions

Paper previously used in printing conductive features was recycled and remade into conductive paper to serve as one layer of capacitor. During the preparation of recycled conductive paper, it is crucial to match the amount of paper fibers to the amount of graphite pigment. Large amount of conductive filler will not necessarily result in more conductive paper. The cellulose fiber network needs to trap the graphite. Overloading will result in dusting and wasting of costly conductive material. Experiment resulted in construction of functioning parallel plate capacitor.

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