

# Contacting paper-based supercapacitors to printed electronics on paper substrates

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**KEYWORDS:** Printed Electronics, Paper Electronics, Supercapacitors

**SUMMARY:** Hybrid printed electronics, in which printed structures and silicon-based components co-exist will likely be among the first commercial solutions. In this case the paper substrate acts much in the same way as circuit boards, containing conductive tracks and acting as a carrier for the electrical components. It is important to consider the contacting of the components to be able to produce low resistance electrical contacts to the conductive tracks. Supercapacitors are able to deliver a large amount of current in a short time and are a good option for short term energy storage and if the printed product is to be used only one, or a few times, it can be the only power source needed. When manufacturing printed electronics, the overall resistance of the printed tracks as well as the contact resistance of the mounted components will add up to the total resistance of the system. A high resistance will cause a voltage drop from the power source to the component. This will waste power that goes to Joule heating and also the voltage and current available to components may be too low to drive them. If the intention is to use a power supply such as batteries or solar cells this becomes a limitation. In this article have been tested several conductive adhesives used to contact paper based supercapacitors to ink jet printed silver tracks on paper. The best adhesive gives about 0.3  $\Omega$  per contact, a factor 17 better compared to the worst which gave 5  $\Omega$ . The peak power that is possible to take out from a printed system with a flexible battery and super capacitors is about 10 times higher than compared with the same system with only the battery.

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Comparing printed electronics on paper substrates to printed electronics on plastic or other high temperature durable and chemically resistant substrate types, clearly shows the more limited possibility to manufacture components directly on the paper substrate. It will be difficult to manufacture all of the components that today

are manufactured on plastics on paper, instead it is likely that hybrid solutions, in which printed structures and silicon-based components co-exist will be among the first commercial solutions (Bidoki et al. 2007; Nilsson et al. 2011; Ren et al. 2010; Carter et al. 2003).

When using paper substrates for hybrid printed electronic solutions the paper will carry conductive tracks and act as a carrier for the electronic components. It is important to consider how to efficiently mount different types of components onto paper substrate and at the same time create low resistance electrical contacts to the conductive tracks (Tobjörk et al. 2011; Smith et al. 2006; Perelaer et al. 2008).

What type of power supply to use is an important part to consider because it determines the possible power delivered and lifetime of the product. The use of standard batteries will be problematic when it comes to printed circuits on paper. Main issues will be the battery size, its flexibility and its environmental impact. An alternative to standard batteries are printed and flexible batteries. However, one of their drawbacks is that they only deliver currents in the range of some mA (Ferreira et al. 2009). This is suitable for some electronics, but certain circuits, such as radio transmitters, may require a higher current under a short time period. For example it could be a wireless sensor node that once every day sends measured data.

The alternative is to use several batteries. A more interesting and suitable alternative is the paper based supercapacitor, which several research groups have shown (Vivekchand et al. 2008; Stoller et al. 2008; Emmenegger et al. 2003; Chu and Btaatz 2002). Supercapacitors are able to deliver a large amount of current in a short time and are a good option for short term energy storage and depending on the estimated useable life time of the printed product could also be the only power source needed. They could be charged by a flexible primary battery, a solar cell, a piezo-electric generator or other method, after which they could deliver a short peak power to for example a radio transmitter that intermittently transmits. Inexpensive materials like graphite and charcoal can be used, hence the device can become very cost effective.

Manufacturing reliable contacts between the printed conductive wire structure on the paper substrate and the electrodes of such supercapacitors is one of the challenges for paper based electronics. The traditional soldering production processes developed for traditional electronics is generally not suitable for paper based substrates. Here is addressed the problem of contacting supercapacitor devices to printed conductive tracks on paper substrates. To produce reliable and low resistance contacts between the supercapacitors and the printed conductive tracks on paper different conductive adhesives

were examined. When considering manufacturing of such systems, low costs and roll to roll production capability are other desirable properties.

## Materials and Methods

The supercapacitors in this article consist of two electrodes, a separator and an electrolyte. They are stacked as shown in the schematic view displayed in *Fig 1*. (top) The separator, a filter paper, is placed between two graphene electrodes to avoid short circuit. Graphene was used as porous material for the electrodes. The large surface area of the graphene layers is particularly suitable for use in supercapacitors since the capacitance scales with the surface area accessible by the electrolyte. Approximately 15 ml of a graphene dispersion ( $c=0.4$  g/l) was filtrated onto a filter paper. After drying in a closed petri dish the graphene film was peeled off from the paper. Pieces of the graphene film with a size of  $1\text{cm}^2$  were used as electrodes in the supercapacitors. The electrodes and the separator were soaked in an electrolyte consisting of aqueous potassium hydroxide. The stacking is contacted with graphite and sealed by laminating it with plastic foil. In the bottom of *Fig 1* is shown a photo of an assembled capacitor.

Graphite sheets were chosen for capacitor electrodes because their electrochemical potential is close to graphene and pseudo capacitances are thereby avoided.

The ink used in this article is the Silverjet DGP-40LT-15C (Advanced Nano Products, South Korea) with a solid content of about 40-45 wt% silver, a viscosity of 16 cP and a curing temperature of 100-150 °C according to the manufacturer. The silver nano-particles have a diameter of approximately 30 nm according to SEM and AFM analysis and are dispersed in Triethylene Glycol Monoethyl Ether. Nano particle inks needs to be sintered after print to reach high conductance. This can be done

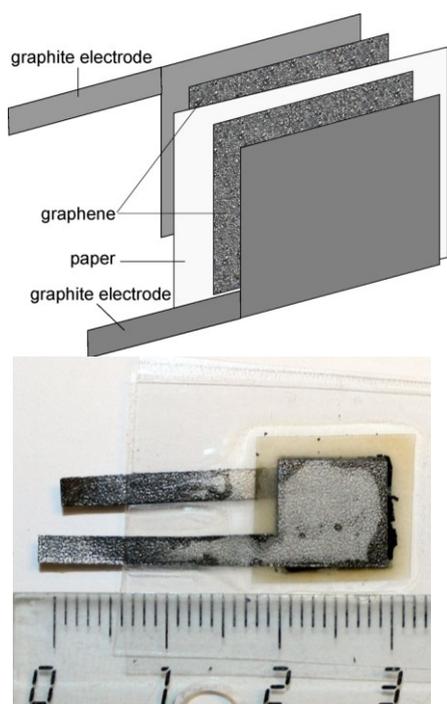


Fig. 1. Schematic view (top) and image (bottom) of paper based super capacitor.

by thermal heating in an oven, by electric sintering or by other methods (Hummelgård et al. 2011; Öhlund et al. 2009; Magdassi et al. 2010; Greer et al. 2007; Perelaer et al. 2006). The printer used was a Dimatix 2831 piezoelectric materials printer, with a 10 pL Dimatix 11610 cartridge (Fujifilm, USA).

A conductive test pattern consisting of two lines with a gap in between was ink jet printed on Canon PT-101 and HP Advanced photo paper. After printing the test structures were sintered for 20 minutes in an oven at 110°C.

Tests were performed by mounting both strips of the same graphene as used in the supercapacitors and complete supercapacitors to the printed silver tracks with various conductive tapes and glues, as presented in *Table 1*. The resistance values in the table are given as specified by the manufacturer. The tape was mounted using tweezers to apply some force, estimated to 550kPa.

The electrodes were made out of 70µm thick graphite sheets (Panasonic EYGS091207) with a specified conductance of 10000 S/cm. The electrodes and printed silver are overlapping 15mm. After mounting the resistance was measured with the 4-wire method with a Keithley 2400 source meter. The probes used was four regular multimeter type probes. They were pressed with enough force to make a good contact to the material but did not damage the surface. The probes were positioned just at the end of the 15mm overlap on each side on the silver or the carbon electrode, as shown in *Fig. 3*. In this way the resistance of the carbon sheets and silver print should be the smallest possible and the measurement should mainly show the resistance of the connection between the materials. The extra added resistance from the carbon and silver is very small, considering it will be a distributed resistance over a  $45\text{mm}^2$  area. The resistivity of the carbon sheets is  $10^{-4}\ \Omega\text{cm}$  and the printed silver in the order of  $10^{-5}\ \Omega\text{cm}$  or less. This gives that the resistance of a  $15\times 3\text{mm}$  strip of carbon is  $0.7\ \Omega$  and that of silver also  $0.7\ \Omega$ , which is about 700nm thick as measured by AFM. Considering that the resistance is measured close to the adhesive, and that the current does not go lengthwise the whole strip of material, but instead through it, it can be reasonable to assume that the added resistance is insignificant. See *Fig 2* and *Fig 3* for the layout and dimensions of the test pattern.

As a demonstration of the possibilities of using supercapacitors to increase electrical power momentarily a demo setup was produced. It consists of three supercapacitors mounted in series, to be able to withstand 3V, using silver epoxy on a Canon PT-101 paper with printed silver nano particle ink tracks. A flexible battery (Enfucell, Finland) was mounted with silver epoxy from the battery contacts to a copper tape to ensure good contact, and on the other side the copper tape creates contacts to the printed tracks. A push button connecting the circuit to the resistor were mounted using anisotropic tape and a load resistor was soldered on wires mounted with copper tape. The total resistance of the printed tracks including contacts is about 4.5 Ω. The supercapacitors were then charged with the battery until they reached the same voltage as the battery, 3V.

The voltage over the load resistor was measured using a National Instruments NI-USB 6009 DAQ at a sampling speed of 1kS/s. The battery and the capacitors have different inner resistances and will perform differently with different loads. Therefore different values of the load resistor was chosen for each case, 175  $\Omega$  for the battery and capacitors and 22  $\Omega$  for the battery only. This gives a more realistic comparison, otherwise one of the cases will not show the best possible power delivery. The power was calculated using the voltage drop over the resistor and the known resistor.

## Results

In Fig 4 and Fig 5 are shown photos of the ink jet printed test structures with graphite electrodes mounted with the adhesives as described in Table 1. The measured resistance of the test patterns after mounting is displayed in Fig 6. The adhesive numbers on the x-axis are specified in Table

Table 1. List of conductive adhesives used

Type of Adhesive	Product name	Specified resistance	Nr.
Conductive silver epoxy glue.	CW2400, Chemtronics	< 0.001 $\Omega$ cm	1
Double-sided copper tape with conductive acrylic adhesive. (isotropic)	Laird Technologies	< 0.1 $\Omega$ Through tape	2
Anisotropic (z-direction) conductive particle tape.	nr. 9705, 3M	< 0.3 $\Omega$ Contact resistance	3
Isotropic conductive fiber tape.	nr.9713, 3M	0.5-2.5 $\Omega$ Contact resistance	4

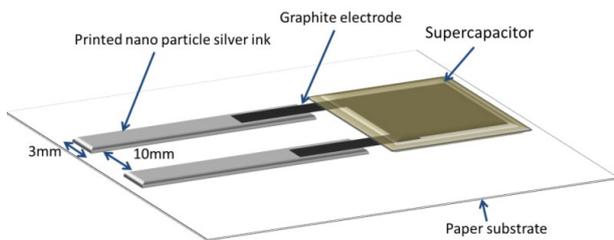


Fig 2. Layout of the inkjet printed test pattern with mounted supercapacitor.

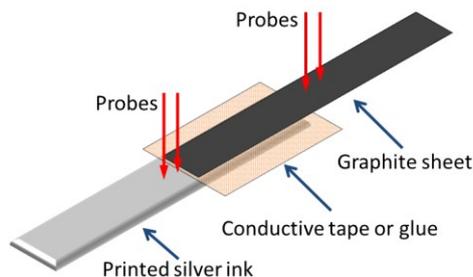


Fig 3. Schematic showing the mounting of electrodes with conductive tape or glue and the position of the four measurement probes.

1. It can be seen that the resistance values are similar for test structures mounted with the same type on adhesive on HP and Canon paper.

The standard deviation, as indicated by error bars in the graph, show that the largest resistance spread is for copper tape (adhesive 2) and the smallest for silver epoxy (adhesive 1). The lowest resistance for both papers is achieved by using the silver epoxy.

An image of the demo setup is shown in Fig. 7 and the results from the power measurements performed on the setup are shown in Fig. 8. Here, the power over the load resistor is displayed as a function of time after the supercapacitors have been charged with a 3V flexible battery. The calculated capacitance from the measurements is about 5 mF for the three serial coupled supercapacitors, which gives about 15 mF for each. Using the paper based super capacitors with the battery show that it is possible to supply about 10 times higher peak power.

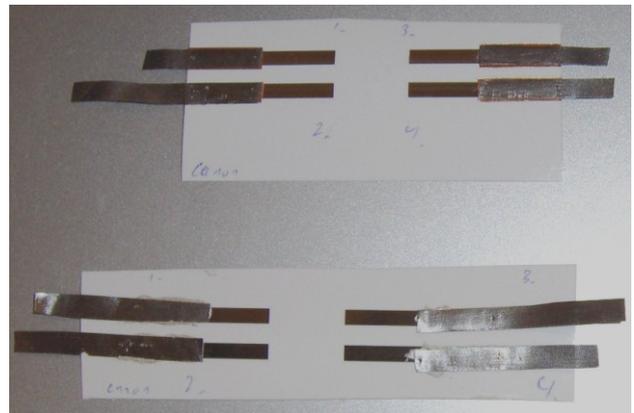


Fig. 4. Photo of printed nano silver particle ink structures printed on photopaper with graphite electrodes mounted with copper tape (top) and silver epoxy (bottom).

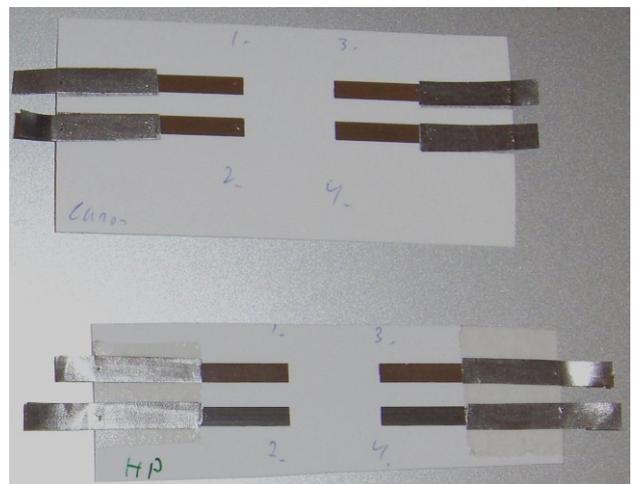


Fig. 5. Photo of printed nano silver particle ink structures printed on photopaper with graphite electrodes mounted anisotropic conductive tape (top) and anisotropic conductive tape (bottom).

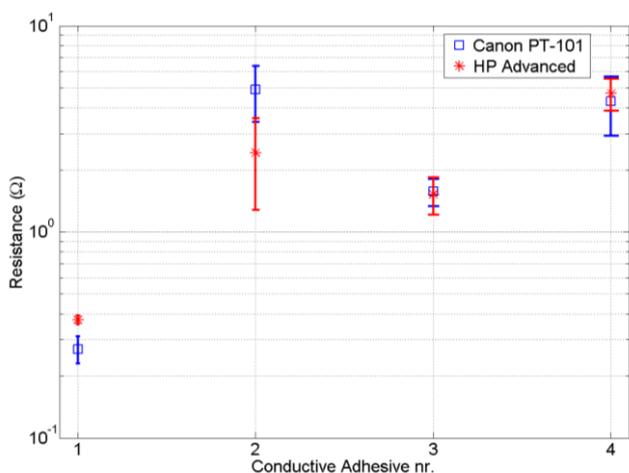


Fig 6. Resistance measurements from the graphite electrode to the printed silver with standard deviation indicated with error bars, adhesives are; silver epoxy (1), double sided copper tape (2), anisotropic tape, (3) and isotropic tape (4).



Fig 7. Image of the demo setup containing three supercapacitors mounted on printed silver ink tracks.

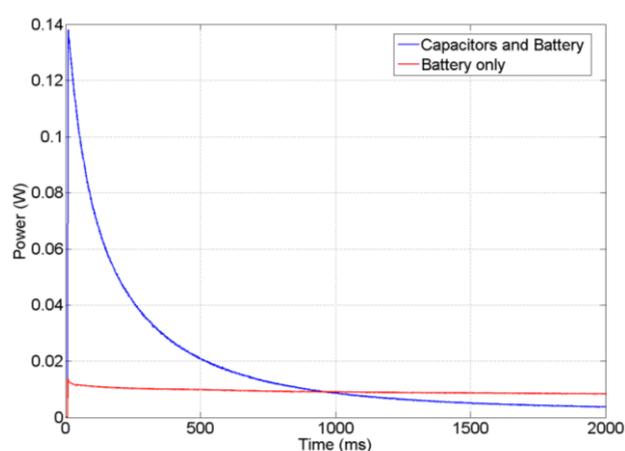


Fig 8. Relative power output over a load resistor vs. time for three supercapacitors in series and charged by a flexible 3V battery (Enfucell) compared to power delivered only by the battery.

## Discussion

The materials used for contacting electrodes each have some advantages and drawbacks, some more important if they are to be used in large scale fabrication. The conductive epoxy has the benefit of resulting in mechanically stable contacts that will not peel off easily and also shows the lowest resistance of the adhesives tested here. The drawback is that the application of such glue onto the substrate can be somewhat difficult because of the high viscosity and the risk of short circuit conductive lines if smeared onto nearby conductors. Also the pot life of such glue is quite short after mixing. The glue should also be hardened at an elevated temperature, 60-120°C, to get the best result.

The benefit of using anisotropic tape is that it can cover several conductive tracks without risk of short-circuit, the tape is only conducting in the z-direction because it uses conductive particles that are not laterally in contact. This makes application onto the substrate much easier, and the resistance of the electrode connection is shown to be the second lowest achieved. The drawback is that the surfaces should be very smooth and the two surfaces being joined should be pressed together otherwise conduction is not achieved. The mechanical stability is not as good as with epoxy and a small separation, even some  $\mu\text{m}$ , will increase resistance dramatically.

Isotropic tapes, both the copper and conductive fiber, have the drawback that they could short-circuit tracks, so the mounting must be done with smaller pieces of tape. This makes them more difficult to use in automated mounting. The copper tape is quite thick because it consists of a copper film with conductive adhesive on both sides. The copper tape also exhibits the largest standard deviation in the test and overall the copper and isotropic adhesives have the largest resistances in the test.

It can also be interesting to consider the flexibility of the adhesives used, because they are meant to be used on flexible substrates. The tapes will be flexible enough to be bent without problem, however especially the anisotropic tape can lose contact if the mounted components is not as flexible as the paper thereby creating gaps when bent. Using epoxy glue, the bond is stronger than with tapes, but if bent too much will crack. In this article the contact area is 15mm long, and if the construction is expected to be bent a considerable amount, it is recommended to make smaller area contacts.

Also, in practical applications the limiting factor would most likely be the flexibility of the component being attached to the substrate. If for example a rigid chip package is mounted the flexibility is limited by the size of that component, while if more flexible components, such as printed devices, is used the overall flexibility of the system would be higher and then the adhesive used can be the limiting factor. These are factors that should be taken into account for each application, and some trade off will be necessary depending on the most important parameter for the specific case, lowest possible resistance, highest flexibility or manufacturing concerns.

The resistance from the best contacts achieved in this survey will add about 0.3  $\Omega$  per contact compared to 5  $\Omega$  for the worst. This difference is not negligible, all

resistance will add to the total resistance of the circuit. For example, the demo circuit shown in Fig. 7 have a total resistance of 4.6  $\Omega$ , and if some other adhesive was used for contacting the capacitors and battery, resistance could be much higher. When looking in Fig. 6, another choice of adhesive could have added as much as 5  $\Omega$  per contact instead of 0.3  $\Omega$ , which would result in 40  $\Omega$  for the three capacitors and battery instead of 2.4  $\Omega$  for silver epoxy. In comparison a device manufactured out of regular circuit board with soldered components would have a total resistance of < 1 $\Omega$ .

The resistance of the printed tracks naturally depends strongly on the print technique, the ink and the width and thickness of the tracks. In general a value of 0.1-1 $\Omega$  per cm of track can be expected for ink jetted nano particle silver ink tracks. Overall, the resistance of a printed system is much higher than a traditional copper circuit board, and will be a limiting factor when producing circuits. Therefore it is important to try and optimize all parts of the circuit in terms of resistance.

## Conclusions

When manufacturing printed electronics, the resistance of the printed conductive tracks as well as the contact resistance of the mounted components will add up to the total resistance of the system. A high resistance will cause a voltage drop from the power source to the component. This will waste power that goes to Joule heating and also the voltage and current available to components may be too low to drive them. If the intention is to use a power supply such as batteries or solar cells this becomes a prohibitive limitation. In this article have been tested several conductive adhesives to contact paper based supercapacitors to ink jet printed silver tracks on paper. The best adhesive, silver epoxy, gives about 0.3  $\Omega$  per contact, a factor 17 better compared to the worst, copper tape, which gave 5  $\Omega$ . Therefore it can be concluded that the choice of conductive adhesive is very important to keep the resistance of the circuit as low as possible. In some instances an anisotropic tape could be a better choice to avoid the risk of short circuit between nearby tracks and easier application in an automated process.

The difference in peak power that is possible to take out from a printed system with the super capacitors is about 10 times higher than compared with the same system with only the battery.

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