

Supercapacitors with graphene coated paper electrodes

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SUMMARY: Paper based supercapacitors are prepared by stacking a paper between two graphene electrodes and soaking these in an aqueous electrolyte. We demonstrate that supercapacitors can easily be manufactured by using proven paper technologies. Several different electrode materials were compared and two types of contacting material, silver and graphite foil were tested. The influence of the paper used as separator was also investigated.

The supercapacitors with a graphene-gold nanoparticle composite as electrodes showed a specific capacitance of up to 100 F/g and an energy density of 1.27 Wh/kg. The energy density can further be increased by using other electrolytes. The silver contacts showed a pseudo capacitance, which the graphite contacts did not. The papers tested had a minor effect on the capacitance, but they have an influence on the weight and the volume of the supercapacitor.

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Many technologies and applications require energy storage systems that can store and deliver large amounts of energy quickly. The power delivery is often more important than the amount of stored energy. In these situations batteries are less suitable because they perform faradaic reactions and thus have a relatively slow energy transfer (Linden 1995). Supercapacitors are based on electrostatic charge separation (Conway 1999) and therefore show much faster charge-discharge cycles. Furthermore, supercapacitors have a higher power density and a significantly longer cycle life compared with batteries. These are important advantages when it comes to long term applications and cases where current peaks are expected. Supercapacitors are today available as energy storage devices in various sizes, all the way from devices in electronic applications to parts in vehicle power supplies. However, their uses are hampered by their relatively high price.

Conventional supercapacitors are produced using porous conductive substances as electrode materials. Com-

mon materials are various forms of carbons (Davies, Yu 2011). Activated carbons are mostly used as material for electrodes (Pandolfo, Hollenkamp 2006). Carbon nanotubes are also tested and show a great electrical performance (Oya, Ogino 2008; Signorelli et al. 2009). Since A. Geim published his work about graphene (Morozov et al. 2004), many research teams work on graphene electrodes for supercapacitors (Weng et al. 2011; Vivekchand et al. 2008; Stoller et al. 2008; Du et al. 2010). Graphene shows extraordinary electrical properties and can be produced from graphite, an inexpensive raw material. An interesting carrier material for electrodes is paper (Pushparaj et al. 2007; Hu et al. 2009; Hu et al. 2010; Weng et al. 2011; Zheng et al. 2011). Paper can also be used as an ion permeable separator in the middle of the supercapacitor. Compared with traditional materials, paper and graphene have advantages: They can increase the capacitance and they have the potential to produce supercapacitors more cost effective. Another advantage is that thin and flexible supercapacitors can be designed with this approach. Therefore we studied methods to prepare paper-based supercapacitors with graphene electrodes.

Materials and Methods

Preparation of Materials

L(+)-Ascorbic acid (AnalaR Normapur, VWR), potassium hydroxide (pure, Merck), filter paper (00H, Munktell), graphite foil (Pyrolytic Graphite Sheet, 0.025 mm thickness, Panasonic) and poly(vinyl alcohol) (80% hydrolyzed, $M_w \sim 10000$, Aldrich) were used as received. Silver foil (99.9%, 0.025 mm thickness) was purchased from Sigma Aldrich. The foil was cleaned prior to its use by rinsing it with ethanol and deionized water. A sample of thermally expanded graphite was received from Superior Graphite. Samples of greaseproof paper were received from Nordic Paper.

Five different graphene coatings were prepared: chemically reduced graphene oxide (CRGO), dispersed graphite (GSS), two graphene-gold composites (CRGO+Au and GSS+Au) and dispersed graphite in polyvinyl alcohol (GSS/PVA). All electrode materials were filtrated on filter paper. Furthermore, we tested the chemically reduced graphene oxide (CRGO), the graphene-gold composite (CRGO+Au) and the dispersed graphite in polyvinyl alcohol (GSS/PVA) as free standing films. A certain volume of the CRGO+Au composite was annealed at 400°C on pre-shaped charge collectors. A direct comparison of the coated samples with the annealed composite material is not feasible because the composite was directly annealed on the charge collectors and was not filtrated on filter paper. This changes the dimensions of the supercapacitor and thus has an influence on its performance.

Prior to these experiments we produced dispersed graphite by exfoliating expanded graphite in a solvent.

The exfoliation was processed by using a bath sonicator (Branson 5510, 40 kHz) for 3 hours and a probe sonicator (Vibra Cell, High Intensity Ultrasonic Processor, Sonics & Materials INC., 750 W, 20 kHz) for 15 min. The sample was cooled in an ice bath during the probe sonication in order to achieve a better exfoliation effect. We observed in previous experiments that uncooled dispersions still contain agglomerates after the probe sonication. The probe sonicator was set to an amplitude of 30% and a pulsed mode which interrupts the sonication process every eighth second for one second. Approximately 15 to 30 ml of the dispersion was filtrated on filter paper. Finally, the film was slowly dried at room temperature in a closed petri dish. From previous experiments we know that a fast drying process can lead to cracks in the coating.

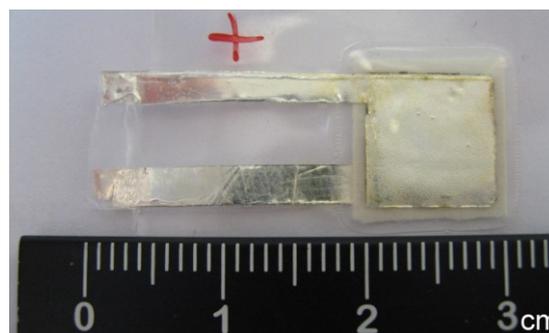
Furthermore, we produced graphene oxide by following Kovtyukhova's method (1999) which is based on Humers method (1958). Afterwards we reduced the aqueous graphene oxide ($c=0.4$ g/l) with ascorbic acid ($c=25$ g/l, ratio 1:1) at 80°C for 20 hours. The reduced graphene oxide was exfoliated by sonicating it in a bath sonicator for 3 hours and applying a probe sonicator for 15 min. We followed the same method as described above for the dispersed graphite. Between 15 and 30 ml of the chemically reduced graphene oxide was filtrated on a filter paper (diameter of filtrated area=3.6 cm). The prepared graphene film was washed by filtration with approximately 1 l deionized water to remove remaining ascorbic acid. Finally, the coated paper was dried in a closed petri dish to ensure an intact coating. Additionally, free standing graphene films were prepared by peeling off the graphene films from the filter paper.

We produced the composites by depositing gold nanoparticles on the graphene oxide and on the dispersed graphite, using the method described in (Zhang 2009).

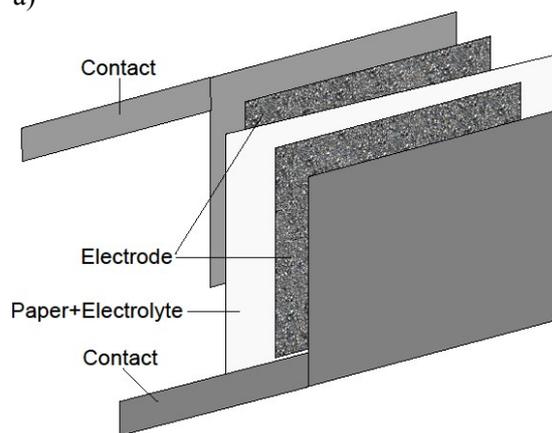
The GSS/PVA electrodes were made by adding 3 g thermally expanded graphite (Superior Graphite) to 100 ml of solvent and stirring with a disintegrator (Dispermat, VMA-Getzmann GmbH) at 25 W for 5 min. 0.75 g of poly(vinyl alcohol), PVA, was dissolved under gentle stirring in 100 ml distilled water. The PVA was added to the graphite suspension and sonicated for 30 min with a probe sonicator (amplitude of 30% in pulsed mode) and left under agitation over night in an open beaker. After 16 hours evaporation the volume had reduced to approximately 100 ml. The sample was sonicated with a probe sonicator for 30 min. 2 g of the suspension was diluted with distilled water to 100 ml and filtrated on filter paper. The graphite was easily peeled off from the filter, giving highly flexible electrodes.

Preparation of Supercapacitors

Supercapacitors were prepared by stacking graphene electrodes, a separator and contacts together, see Fig 1. The separator is a filter paper which was soaked in aqueous potassium hydroxide ($c=7.5$ M). Silver or graphite foil were used as charge collectors. The stack was sealed by laminating it with plastic foil or by inserting the stack between two microscope glasses, held together by two small clamps. A compact stacking is necessary to ensure a stable connection between all components.



a)



b)

Fig 1. Image of a supercapacitor (a) and schematic picture of the stacking of supercapacitor components (b)

Measurements

Measurements were conducted according to the guidelines of Stoller (2010). For first measurements of the supercapacitors capacitance we used an Agilent 34405A $5\frac{1}{2}$ Digit Multimeter and a Hameg HM8143 arbitrary power supply. In order to plot charge-discharge cycles at a constant current, a LabVIEW-based PXI system was used. Together with self-built electronics this functions as a current source for measurements in the range of μA to mA .

The capacitance of a supercapacitor was determined by charging the device with constant current to the maximum operating voltage V_{max} and plotting the discharge curve at a constant current. The maximum operating voltage of supercapacitors with aqueous electrolytes is limited to 1.23 V due to the electrolysis of water at this voltage. The devices in this article were cycled between 0 V and 1 V. Most supercapacitors are operated between $\frac{1}{2} V_{\text{max}}$ and V_{max} and thus this interval of the discharge curve was chosen for calculating the capacitance. In general it is important to calculate the discharge slope in the voltage range that will be cycled according to the desired application because the capacitance is inversely proportional to the voltage. Ideally, the charge and discharge curves are linear. Although the discharge curves of the tested devices are expected to be linear, the upper half of the curve was used for calculating the capacitance. The slope of the discharge curve dV/dt was calculated by applying Eq. 1. t_2-t_1 is the time interval of the voltage drop between $\frac{1}{2} V_{\text{max}}$ and V_{max} .

$$\frac{dV}{dt} = \frac{(V_{\max} - \frac{1}{2}V_{\max})}{(t_2 - t_1)} \quad [1]$$

Afterwards the capacitance C was calculated by dividing the applied current I by the slope of the discharge curve dV/dt , see Eq. 2. All capacitors were charged and discharged with 0.5 mA.

$$C = \frac{I}{\frac{dV}{dt}} \quad [2]$$

The specific capacitance C_s of a supercapacitor was calculated by dividing the capacitance C by the mass of graphene of both electrodes m . This term was further multiplied by four to obtain the capacitance per weight for just one electrode, see Eq. 3. The factor 4 derives from the electrical double layer at the electrode interface forming one capacitor on each electrode (Atkins, De Paula 2006). Thus each supercapacitor consists of two capacitors connected in series.

$$C_s = 4 \cdot \frac{C}{m} \quad [3]$$

The energy E that can be stored in a supercapacitor was calculated by multiplying the capacitance C by the voltage V to the power of 2 and by dividing the whole term with 2, see Eq. 4. Thus the maximum operating voltage, depending on the type of electrolyte, has a great influence on the amount of energy that can be stored.

$$E = \frac{1}{2} \cdot C \cdot V^2 \quad [4]$$

The energy density E/m in Wh/kg was calculated by dividing the energy E by the mass of all cell components m_{cell} .

The sheet-resistance of the graphene coated papers was measured with a Hewlett Packard 3457A Multimeter, which was set to four-point probe mode. All measurements were accomplished at constant conditions in a conditioning chamber run at 23°C and a relative humidity of 50%. To ensure constant conditions for all papers, the samples were placed in the conditioning chamber for 30 minutes prior to the measurements. The sheet-resistance is measured on 10 different areas on the sample and the arithmetic average was calculated.

In order to determine the influence of the separator thickness and the type of paper used as separator on the electrical performance of the supercapacitor, two different papers were tested, filter paper and greaseproof paper. As filter paper the grade 00H (Munktell) with a grammage of 80 g/m², a pore size of 1–2 μm, a thickness of 150 μm and a density of 535 kg/m³ was used. Greaseproof paper (sample from Nordic Paper) with a grammage of 40 g/m², a thickness of 45 μm and a density of 900 kg/m³ was tested. We assembled supercapacitors with one to four separators of each kind. Afterwards we measured the capacitance of the supercapacitor and plotted the average of five measurements against the separators grammage.

Results

The charge/discharge curves were evaluated with regard to their curve progression and the resulting capacitance. All samples showed an almost linear behavior, see Fig 2.

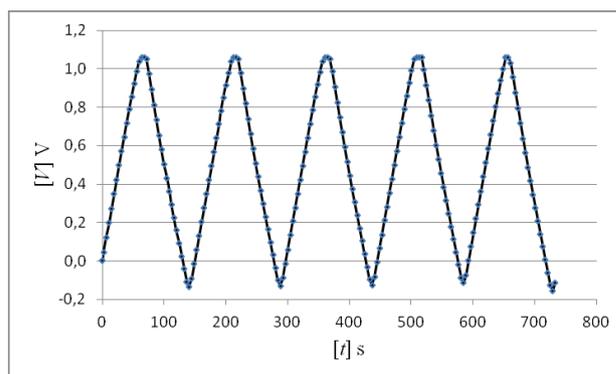


Fig 2. Charge discharge curves of a supercapacitor with GSS/PVA electrodes

Table 1. Sheet-Resistance of electrode materials and properties of supercapacitors depending on electrode materials

Material	[R _s] Ω/sq	Paper electrode	[C] mF	[C _s] F/g	[E/m] Wh/kg
CRGO	99.8	✓	58.3	49.41	0.22
CRGO+Au	1761		300	80–100	1.27
GSS	13.2	✓	0.35	0.25	0.001
GSS+Au	403	✓	11.6	9.84	0.049
GSS/PVA	0.3		5.6	0.8	0.008

Measurements of different supercapacitors showed capacitances of up to 0.3 F, see Table 1. This value was measured for discrete graphene-gold composite electrodes with a size of 1 cm² each. We calculated a corresponding specific capacitance of 100 F/g and an energy density of 1.27 Wh/kg.

Compared with the other electrode materials the annealed composite material (CRGO+Au) shows superior performance. The graphene (CRGO) electrodes show a good performance too, but are not as good as the composite. The dispersed graphite (GSS) shows a significant lower capacitance than the other materials. However, dispersed graphite shows a low sheet-resistance, see Table 1. A benefit of dispersed graphite is that the production process avoids the classical oxidation and reduction steps. The addition of gold nanoparticles to the dispersed graphite (GSS+Au) significantly enhances the capacitance of the electrodes. In contrast to that, the sheet-resistance of both composites is higher than the value of the base material. Cracks were visible in the coating layer causing the high resistance. The modified dispersions do not form closed coating layers after the final drying. Small cracks were formed during the drying process. The GSS/PVA material forms a dense film resulting in the lowest sheet-resistance. Since all cell components contribute to the supercapacitors series resistance, an electrode material with a low resistance is desired. Measurements regarding the supercapacitors separator are presented in Fig 3. The capacitance of the supercapacitors is plotted against the grammage of the paper used as separator. The graph visualizes that in this case the capacitance neither correlates with the paper grammage nor with the type of paper.

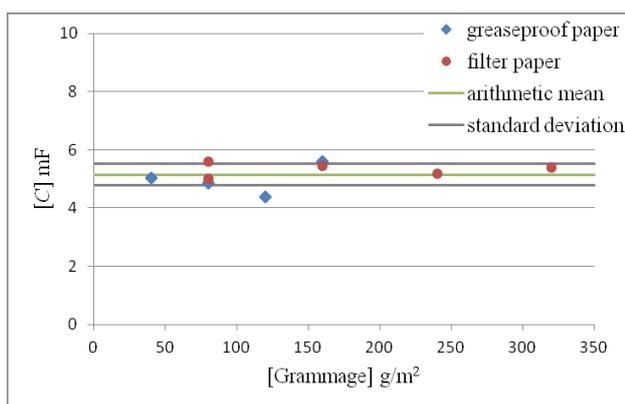


Fig 3. Influence of grammage and type of paper used as separator on capacitance. Neither the paper nor the grammage seems to affect the capacitance.

For all prepared supercapacitors the measurements indicate high series resistances and leakage currents. Accurate values cannot be stated because of imprecise measurements. The series resistance was caused by all cell components. A large impact had the contact resistance. The supercapacitors showed a pressure dependence, as it was reported by Gourdin et al. (2011). When pressure is applied on top of the supercapacitor, the metal foil contacts are pressed on the electrodes and the contact between the graphene electrodes and the separator is improved. This results in a decreased resistance and an increased capacitance. Moreover, the contact material itself influenced the performance to a great extent. We observed that the silver contacts were oxidized during the cycling of the supercapacitor. Silver is not suitable as contact material for this system (Takeno 2005) due to its oxidation in the cycled potential range at the given pH. First tests of graphite foil as contact showed a stable behavior of the material. Another important factor is the electrochemical window of the electrolyte. The risk of water electrolysis was avoided by cycling the supercapacitor below 1 V.

Discussion

The results demonstrated how the choice of the supercapacitor materials has a great impact on the supercapacitor performance. The electrical performance mainly depends on the electrode composition. Graphene shows a high conductivity and a good performance in supercapacitors. The addition of gold nanoparticles enhances the performance of the electrode material significantly. We believe that the gold nanoparticles act as small spacers between the graphene sheets. If so, the insertion of gold increases the porosity of the coating and thus enhances the capacitance of the supercapacitor. Furthermore the nanoparticles prohibit a restacking of the graphene sheets to graphite. Dispersed graphite has a great potential too, although it does not show large capacitances in supercapacitors. However, its production process is simpler, faster and cheaper than the graphene production via oxidation and reduction. Graphene, dispersed graphite and other materials can be coated on paper or used as filler in paper using proven technologies. The preparation of high concentrated graphene dispersions allows the usage of roll-to-roll production process-

es. In principle the coating of a paper on both sides will further enhance the performance and reduce the material costs of the supercapacitor. The general stacking and the contact material have a great influence on the supercapacitor as well. To avoid pseudo capacitances arising from oxidation of the contacts, silver was replaced by pyrolytic graphite. Tests of the influence of the separator type and grammage showed that the paper has no detectable effect on the capacitance, but the paper will have an influence on the weight and the volume of the supercapacitor.

In future experiments we will test other charge collector materials and electrolytes. To reduce the limiting parameters we must find a compatible combination. Other types of electrolytes can allow operation within a larger electrochemical window, i.e. higher voltage, and thereby enhance the energy density to a great extent, see Eq. 4. Furthermore we will focus on composite materials and study how additives such as nanoparticles can enhance the electrical performance. To compare different materials and stackings a test set-up with controlled conditions must be constructed. It is favorable to control the pressure on the stacking, the size of the layers and the contacting.

Conclusions

Supercapacitors can be prepared by using graphene coated paper sheets as electrode material. The working principle allows a simple stacking of the components. Thus supercapacitors with paper components can be produced by using proven paper making technologies. The main advantages of supercapacitors with graphene-paper electrodes are the scalable low cost production, the inexpensive materials and the large variety of possible applications. These benefits can be achieved because of the combination of excellent paper and graphene properties. The deposition of gold nanoparticles on graphene further increases the supercapacitors capacitance.

Acknowledgements

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