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Pigment-Cellulose Nanofibril Composite and Its Application as a Separator-Substrate in Printed Supercapacitors

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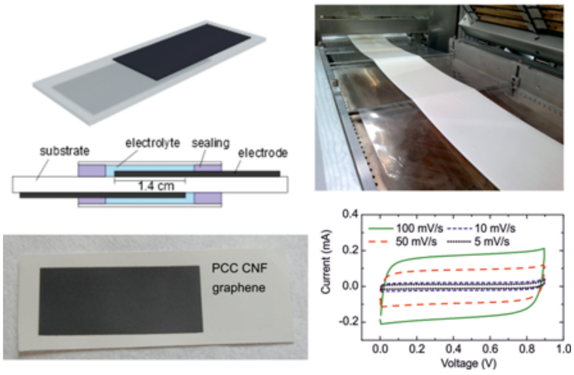
Pigment-cellulose nanofibril (PCN) composites were manufactured in a pilot line and used as a separator-substrate in printed graphene and carbon nanotube supercapacitors. The composites consisted typically of 80% pigment and 20% cellulose nanofibrils (CNF). This composition makes them a cost-effective alternative as a substrate for printed electronics at high temperatures that only very special plastic films can nowadays stand. The properties of these substrates can be varied within a relatively large range by the selection of raw materials and their relative proportions. A semi-industrial scale pilot line was successfully used to produce smooth, flexible, and nanoporous composites, and their performance was tested in a double functional separator-substrate element in supercapacitors. The nanostructural carbon films printed on the composite worked simultaneously as high surface area active electrodes and current collectors. Low-cost supercapacitors made from environmentally friendly materials have significant potential for use in flexible, wearable, and disposable low-end products.

Keywords: cellulose nanofibrils (CNF), graphene, carbon nanotubes, supercapacitors, separator, substrate



1. INTRODUCTION

Here, we present a pigment-CNF composite which has a nanoporous pigment-fiber network structure to enable optimal absorption of ink solvent, but still allow printing on its smooth and closed surface without short circuits. These properties facilitate use of the composite as a separator-substrate in printed supercapacitor applications. The composite suitability for printed electronics applications was demonstrated previously by ink-jet with a silver-nanoparticle ink.[1] It was also modeled and demonstrated that, in addition to the smoothness, the porosity is the most relevant property for the substrate.[2] The optimal porosity and smoothness properties of the substrate are strongly dependent on the printing method, ink, solvent, and target application related to the absorption, surface charge, and binding properties. The selection of raw materials such as pigment, cellulose micro/nanofibrils, ink solvent, and other additives enables varying these relevant properties of the substrate. The production of the composite at laboratory scale is described in.[1] Here, we present the up-scaling method at pilot scale to

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*Corresponding author: Katariina.Torvinen@vtt.fi increase the production possibilities of the pigment-CNF composite.

There has been an increasing interest in developing new types of supercapacitors, also called ultracapacitors, to meet the requirements of various energy storage applications.[3-6] Supercapacitors are rechargeable electrochemical energy storage devices that offer great advantages of high power capability, high rates of charge and discharge, long cycle life, flexible packaging, and low weight compared to other energy storage devices.[7] Future developments are moving toward thin, low-cost, lightweight, and flexible solutions that can be utilized in wearable and disposable electronics applications.[3] The emerging field of energy harvesting applications,[8] for example from light,[9] RF fields,[10] or vibrations,[11,12] is lacking complementary energy storage solutions. The low-cost, flexible, metal-free, non-toxic, and disposable supercapacitors produced by efficient process are needed for application in printed electronics systems.[11,13-15] Nanostructural carbon materials such as carbon nanotubes (CNT) and graphene are promising future materials to be used in supercapacitors, due to their excellent electrical conductivity and high surface area.[7,16-18] Solution-processed supercapacitors prepared from high viscosity CNT inks have been previously demonstrated by the authors.[11,10,14,19] In these cases, a supercapacitor was fabricated so that first, the CNT electrodes were deposited on distinct plastic substrates, and second, a commercial paper separator, soaked with the electrolyte, was sandwiched between the CNT electrodes. In this paper, however, the supercapacitor electrodes are directly printed on the separator-substrate and there is no need for subsequent assembly steps such as lamination.

Inks containing nanostructured carbon materials are usually deposited onto flat and dense substrates such as glass, plastics, or metallic films. However, the use of porous materials, such as paper, has many advantages, such as strong adhesion of ink onto paper, as well as the surface charges and functional groups of the paper material.[20] Paper absorbs solvents easily and binds nanostructural carbon strongly, making the fabrication process simpler than with flat substrates.[21,22] Here, we take advantage of a highly nanoporous cellulose nanofibrils-based substrate in a supercapacitor application.

There are a few previous demonstrations of paper-based supercapacitor architectures.[4,21-25] Hu *et al*. demonstrated a fully integrated printed supercapacitor on a lightweight paper substrate with single-walled carbon nanotubes (SWCNT).[22] The electrodes were deposited on both sides of the substrate, with the paper also serving as a separator; however, to prevent the device from short-circuiting due to the micron-sized pores in the paper, a surface treatment was needed to block the ink from absorbing into the paper. To prevent the supercapacitor electrodes from short circuits, in our study, only calendering for pilot-scale film-casted pigment-CNF substrate was needed. This indicates that nano-sized porosity in the composite enables simpler and roll-to-roll up-scalable manufacturing. Here, we demonstrate an integrated structure in which the pigment-CNF composite is used as both separator and substrate for screen-printed graphene electrodes, as well as spray-coated CNT electrodes. The nano-sized pore structure enables the transport of electrolyte ions through the composite, but at same time does not cause short circuit, though all components are integrated on the same separator-substrate. No metal current collector was used in the supercapacitors. The capacitance and equivalent series resistance (ESR) of the devices were both fairly good, taking into account the rather thin layer of the CNT and graphene inks on the pigment-CNF separator-substrate.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The cellulose nanofibrils (CNF) used in these trials was made of Finnish once-dried bleached hardwood (birch, *Betula L.*) kraft pulp (BHKP). The fibril cellulose, later called VTT CNF (Fig. 1), was obtained after eight passes through Masuko Sangyo's (Supermasscolloider type MKZA10-15J) grinder, using decreasing gap width and increasing operating power. The rotation speed was fixed to 1500 rpm. VTT CNF was used at all pilot-scale test points. In addition to cellulose microfibrils, Celish KY-100g (Daicel Chemicals Ltd., Japan) has been used in samples formed at lab scale.

Pigments used in the pilot-scale trials include plate-shaped kaolin Capin SP (Imerys), coating grade kaolin Capim DG (Imerys), and aragonite-shaped precipitated calcium carbonate (PCC) Opacarb A40 (Specialty Minerals Inc.). Rosette-shaped Albacar PCC (Specialty Minerals), and Intramax 60 kaolin (Imerys) were used in the laboratory scale trials. The plastic carrier material used in the pilot tests was 23 μm

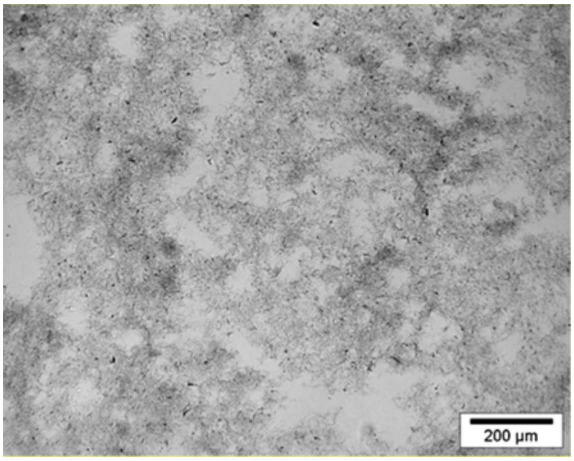

Fig. 1. SEM image of VTT's cellulose nanofibril (CNF) grade.

poly(ethylene terephthalate) (PET) film. The plasma activation was done for the carrier film with an argon/nitrogen blend and 50 W/m^2/min intensity by a Vetaphone Corona-Plus (Type TF-415, CP1C MKI1 2.0 kW) device with speed 5 m/min, before film casting, to increase the surface energy of the PET film.

2.2 Pigment-CNF film fabrication

VTT has used the equipment of Coatema® Coating Machinery GmbH to produce semi-industrial roll-to-roll pilot-scale webs and films. Different coating and drying possibilities are available to be applied as a surface treatment process to the webs and films described elsewhere.[27] In this study, the SutCo environment was used successfully to produce pigment-CNF substrates with 7% dispersions. The dispersions that contained 80% pigment and 20% CNF by weight were first dispersed carefully with vigorous mixing using a Diaf 100WH dissolver for 50 minutes at 400 rpm. The dispersions were then cast at a speed of 2 m/min with a width of 300 mm and a length of 6 - 8 m. After this, the wet-coated film was cut to A4-size samples together with the carrier film, and pressed with blotter papers under 0.8 kg weights to remove the excess water.

After slight initial off-line wet pressing, there was a similar variation in the initial dry content, from 20 to 35%. Drying of PCN substrates was carried out using a contact dryer or in the oven. The contact dryer is shown schematically in Fig. 2. It includes a curved metal plate, heated by electrical coins from the bottom side, and a tensioned dryer fabric. Experiments were carried out at a hot-plate temperature of 60°C for 20 minutes, with a constant fabric tension of 2 kg/cm. A commercial dryer fabric made from flat yarns and with a permeability of 1600 m^3/m^2/h was used. A more detailed drying study was also done and reported in Timofeev *et al.*.[28] The pilot-manufactured PCN sheets were also dried in an oven at 55°C, between glass plates and under 5.6 kPa pressure weights, for 48 hours for some measurements.

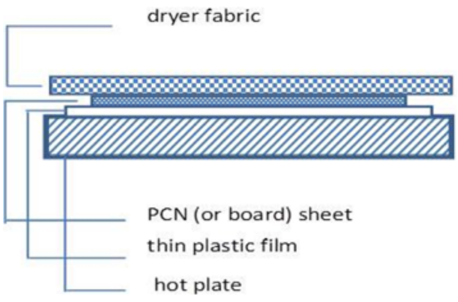

Fig. 2. Schematic view of a contact dryer.

2.3 Pigment-CNF film testing

After drying, the samples were conditioned under a standard climate (25°C, 50% RH) before calendering and physical testing. The sheets were calendered using a laboratory-scale calenderer with hard roll nip once. The calendering was done with approximately 20 MPa pressure and 150°C temperature. Standard characterization methods were used for sheet testing. The grammage of the samples was determined according to ISO 536:1995. The thickness was determined according to ISO 534:1998 and the density was determined based on the measured values of grammage and thickness. Surface roughness was measured using a Dektak 150 Surface profiler (Veeco), with a 2.5 μm probe at 1 mg pressure. R_a is the arithmetic mean roughness, R_q is the root mean squared roughness, and the peak-to-valley value is the height difference between the minimum and maximum points in the measured data.

Thermogravimetric analysis (TGA) was performed using a Mettler TGA 851e thermogravimetric analyzer (Mettler Toledo). The measurements were performed in an air atmosphere and the air flow was 50 mL/min. The heating rate was 100°C/min up to 230 or 270°C.

2.4 Supercapacitor fabrication and characterization

Graphene supercapacitor electrodes were screen-printed on both sides of the substrate using a conductive graphene ink (Vor-ink X103 from Vorbeck). Two layers were screen-printed on each side, and after the printing of each layer, the sample was dried for 2 min at 120°C in the oven. The samples were additionally dried for 10 min at 120°C after all layers had been deposited to ensure proper ink drying. CNT supercapacitor electrodes were spray-coated on both sides of the substrate using a CNT-xylan nanocomposite ink, the preparation of which is described elsewhere.[15] The ink formulation used here was 3.0 wt. % CNT and 1.5 wt. % xylan in water. A PET mask was used to define the electrode area while spray-coating.

Graphene supercapacitors were prepared on the substrates

Table 1. Characteristics of cellulose micro/nanofibrils used in laboratory-scale formed sheets measured by Brookfield: 1.5%, vane spindle V73. Detailed descriptions of viscosity, transmittance, and visual appearance evaluation used for cellulose micro- and nanofibrils are published in Kangas *et al.*.[26]

Sample	Viscosity, mPas·s 10 rpm, 1.5% conc.	Transmittance, % 800 nm, 0.1% conc.	Visual appearance (optical microscopy)
VTT CNF	22502	60.2	Fine
Daicel KY-100G	15777	8.1	Coarse, long fibrils

Table 2. Characteristics of cellulose nanofibrils used in pilot test analysis measured by Brookfield: 1.5%, vane spindle V73.

Sample ID	VTT CNF	STDEV
Cons. [%]	3.42	-
pH	5	-
Apparent yield stress (Pa)	33	1
Viscosity, 0.5 rpm (mPa*s)	152689	517
Viscosity, 10 rpm (mPa*s)	19693	108

Table 3. Pilot manufactured trial points with different pigments.

Trial point	Pigment 80%	CNF 20%
1	Kaolin Intramax	VTT
2	PCC Opacarb	VTT
3	Capim SP mass 50% Capim DG mass 50%	VTT
4	Capim SP	VTT

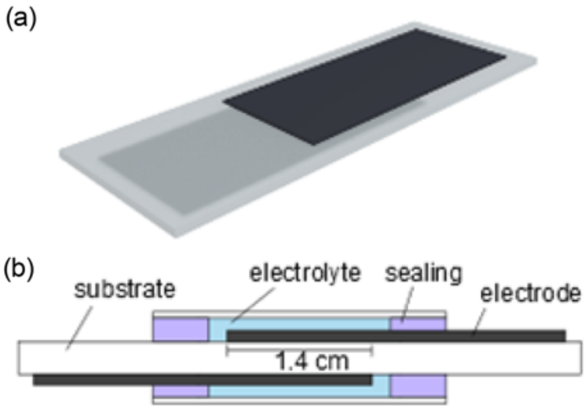

Fig. 3. Schematic overview (a) and cross-section view (b) of the supercapacitor device configuration and assembly.

with three different pigment dispersions (PCC-based TP2 and Kaolin-based TP3 and TP4, details of trial points shown in Table 3). CNT devices were prepared only on the kaolin-based TP3 substrate, as the spray-coating method was observed to be unsuitable for the PCN substrates due to the dilute CNT dispersion swelling the composite, resulting in buckling. The electrodes were 3.2 cm by 1.4 cm with an overlap of 1.4 cm, yielding an active device area of 2 cm^2 (Fig. 3). The active area of the supercapacitor was soaked in aqueous NaCl (1 M) during measurements.

The supercapacitors were characterized in a 2-electrode configuration with a Zahner Zennium potentiostat/galvanostat. Cyclic voltammetry (CV) was recorded from 0 to 0.9 V at voltage sweep rates 5, 10, 50, and 100 mV/s. Supercapacitor properties were determined from a galvanostatic (constant-current) experiment, according to an industrial standard (IEC 62391-1 (2006)). The devices were charged to 0.9 V in 1 min, held at 0.9 V for 30 min, and then discharged with a constant current. The capacitance is calculated from the slope of the discharge curve, and equivalent series resistance (ESR) from the initial IR drop at the beginning of discharge.

3. RESULTS AND DISCUSSION

3.1 Pigment-CNF film material characterization and analysis

The compatibility of the composite substrate with inkjet printing of silver nanoparticle ink and a thermal sintering process was recently demonstrated.[1,2] The conductivity of silver patterns was similar to those printed on PET film. The best conductivity was obtained for silver nanoparticle patterns, which were inkjet-printed on kaolin-based sheets. A curing temperatures as high as 220°C could be used without causing any damage to the sheets. Thermogravimetric analysis (TGA) showed that the substrates can tolerate short exposure to temperatures up to 270°C and over 12 h exposure to 230°C, as shown in Fig. 4. These temperatures are much higher than the current substrates for printed electronics, which enables, for example, high sintering temperatures and an increase in the production speed. In oven tests, it was also observed that PCC-based pigments stand temperatures over 200°C better than kaolin pigments. The kaolin seems to have a tendency to become brittle and dark, probably because of the ingredients involved in the kaolin production process. Similar effects were not seen with PCC grades.

The PCN substrate should meet certain quality requirements in order to be applied as a base for printed supercapacitor applications. The main requirements concern nanoscale porosity, surface smoothness, flexibility, and sufficient strength properties of the substrate. The substrate with kaolin pigment particles, together with CNF, has a suitable structure to be used as a substrate for printed energy storages. The reason for that is the lower porosity compared to the PCC-

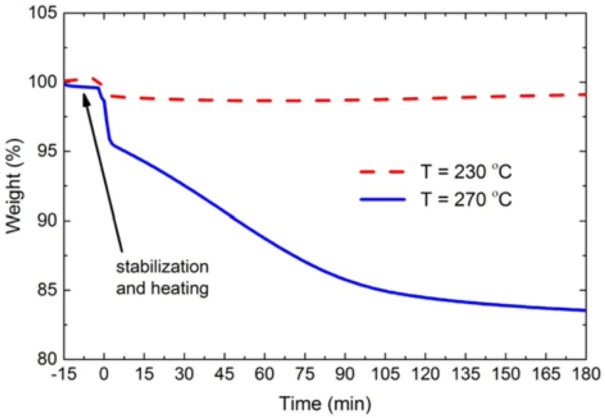

Fig. 4. Thermogravimetric analysis of pigment-CNF sheets shows that the substrate can stand temperatures as high as 230°C (red) for hours.

Fig. 5. A smooth layer of pigment-CNF dispersion was spread on top of the support material.

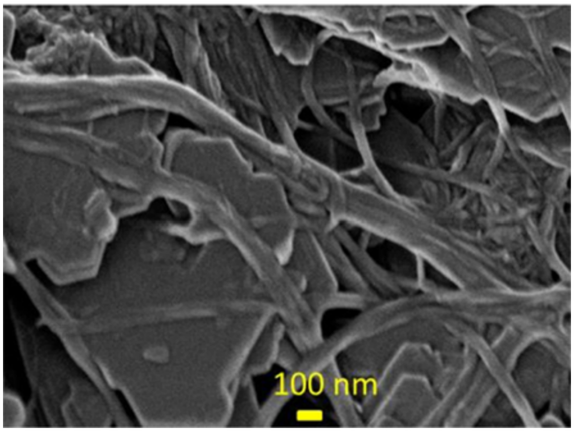

Fig. 6. High resolution SEM image of the PCN sheet before calendering.

based substrates.[2] Several methods of upscaling the production of pigment-CNF substrates (PCN) were tested: vacuum-assisted hand sheet-making, foam forming, solvent casting, and spraying. The most promising way for industrial manufacturing turned out to be solvent casting. The controlled adhesion between the pigment-CNF dispersion and the carrier plastic film and the high consistency of the dispersion (7 wt. %) in film casting turned out to enable excellent properties for pigment-CNF substrate (Fig. 5). The main advantages of the solvent casting method are: 1) prevention of shrinkage of substrate during drying, 2) usage of high consistency (over 7%) dispersion, 3) control of toughness and flexibility of substrate by pressing, and 4) even formation. High resolution SEM images show that porosity of PCN substrates is on a nanoscale, as shown in Fig. 6.

The web was pressed and dried attached to the carrier plastic using different drying methods, as described in Timofeev *et al.*.[28] After drying, the sheets were calendered at laboratory scale. Pigment-CNF dispersion was spread at 7% consistency on the plastic carrier material. The method is based on a filed patent application.[29] The grammage of the final wet PCN sheets varied from ~142 to ~221 g/m^2, and there was a similar variation in the initial solids content in the range of 20% - 35%. Optimizing the drying conditions turned out to be of extreme importance. Quick drying of the pigment-CMF/CNF web resulted in cracks, and the dried structure was hard and brittle. Slow drying at room temperature resulted in a smooth and more flexible structure. The best results were obtained by using pressing of the formed web before or during drying. The smoothest surface was obtained for the sample that was dried in the oven under a weight. Interestingly, the excess water can be easily pressed out of the structure, which clearly speeds up the drying process. Pressing also improved further the flexibility of the formed structure.

The effect of different drying conditions on pilot-scale manufactured PCN sheet properties was studied (Table 4). The smoothest surface obtained when drying was made at 50°C in the oven, under pressure. In these studies of trial point 1, the contact dryer was not included. Based on drying studies, a contact dryer was chosen as the drying method for trial points 2-4.[28] Drying at room temperature resulted in a rougher surface on PCN substrates, as shown in Table 4.

The environmental performance of these products was excellent (Fig. 7). Evaluation was carried out using a standardized LCA approach, including fossil greenhouse gases (CO_2, CH_4 and N_2O), expressed as carbon dioxide equivalents (CO_2 eq). For the reference product (PET film), no water consumption data was available. The following assumptions, based on the experiments, have been made related to the environmental performance of substrates: The composite substrates are compatible with printing methods, such as inkjet, flexo, and screen-printing, and are of suitable

Table 4. The influence of different drying methods on sheet properties at trial point 1. RT = Room temperature.

Pressing & drying at Trial point 1	Thickness, [μm]	Grammage, [g/m^2]	Density, [kg/m^3]	Ra, [μm]	Rq, [μm]	Peak-to-Valley, [μm]
TP1, pressing 10 min, drying +50°C, under pressure	102.0 ± 1.7	143	1398 ± 23	0.15	0.19	1.2
TP1, pressing 10 min, drying RT	161.2 ± 0.3	209	1297 ± 2	0.60	0.70	4.4
TP1 pressing 10 min, drying +50°C	124.7 ± 5.2	178	1425 ± 60	0.20	0.25	2.0
TP1, no pressing, drying RT	179.1 ± 3.0	221	123 ± 21	0.45	0.60	4.0

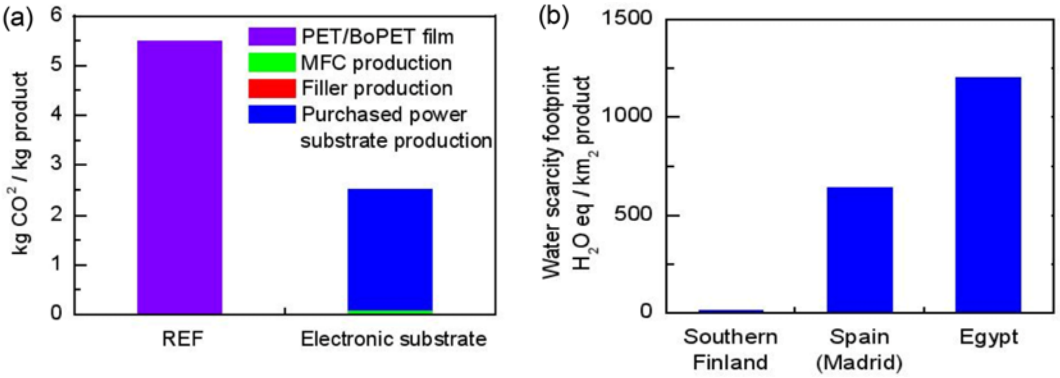

Fig. 7. Environmental performance screening for the substrates of printed electronics: Calculated cradle-to-gate carbon footprint for printed electronics substrate in comparison with PET/BoPET film reference (range 5-8 kg CO2/kg from the literature) (a) and water consumption of substrate production weighted with local scarcity indices (b).

quality for low-cost applications, such as disposable personal electronics and diagnostics applications. In this paper, we report the use of CNF as a cellulose material, but the similar pigment-cellulose composite can also be composed of cellulose microfibrils (CMF).[26] The composite consists of 80% pigment filler (e.g. $CaCO_3$, kaolin) and 20% CMF, and it is formed by vacuum filtration, dried under pressure, and calendered. However, one must note that this concept still requires development, and especially drying conditions are critical.

3.2 Printed nanocarbon supercapacitors on pigment-CNF films

Supercapacitors were prepared on the PCN-calendered substrates of TP2, TP3, and TP4 (Table 3). The calendered substrates were used because it was observed that the uncalendered substrates absorb too much ink, which causes short-circuiting of the electrodes on the opposite sides of the substrate. The adhesion of the ink on the calendered PCC-based TP2 was poor: the layer delaminated as soon as the ink had dried, and so could not be used for supercapacitors (Fig. 8). The sheet resistance of the printed graphene layers, measured using the 4-probe method, was 10 Ω/□, and that of the CNT layers varied between 30 and 70 Ω/□. The large variance of the CNT layer resistance is due to difficulty in depositing layers of similar thickness with a handheld spray-coater.

CV curves of typical supercapacitors are shown in Fig. 9. The CNT supercapacitor had more rectangular curves, whereas the graphene supercapacitor's curves are less rectangular. The presence of a voltage maximum indicates the presence of Faradaic reactions.[30] A possible source of reactive species is the graphene ink, which contains different binders and other additives designed to improve printability. The CNT ink, composed only of carbon nanotubes and xylan polymer,[15] does not have this behavior, but the printability is poorer than that of the graphene ink.

The quantitative properties were determined from galvano-

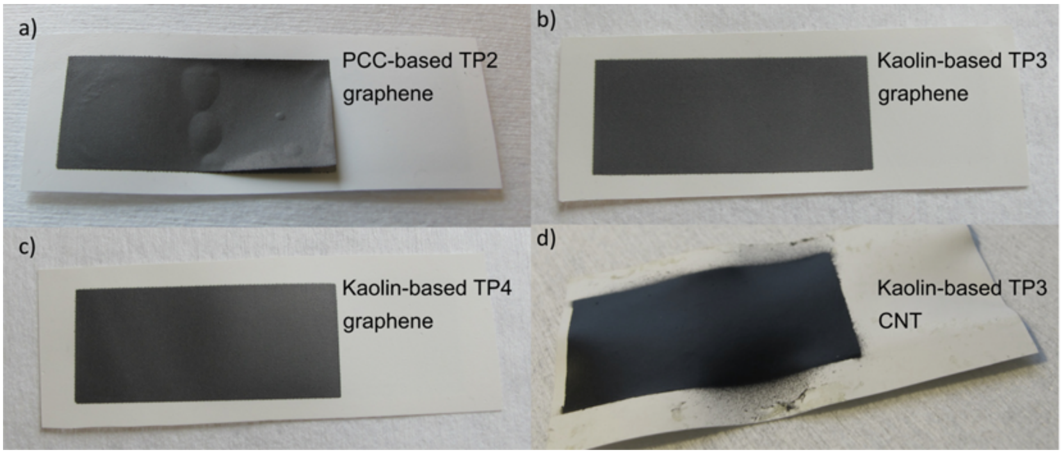

Fig. 8. Printed graphene and CNT layers on the substrates. Good results were achieved for kaolin-based substrates when printed with graphene ink. The adhesion of ink to the PCC-based substrate was poor, resulting in delamination of the printed electrode layer. Spray-coating the CNT ink resulted in the sheet buckling due to absorption and the ink spreading under the mask.

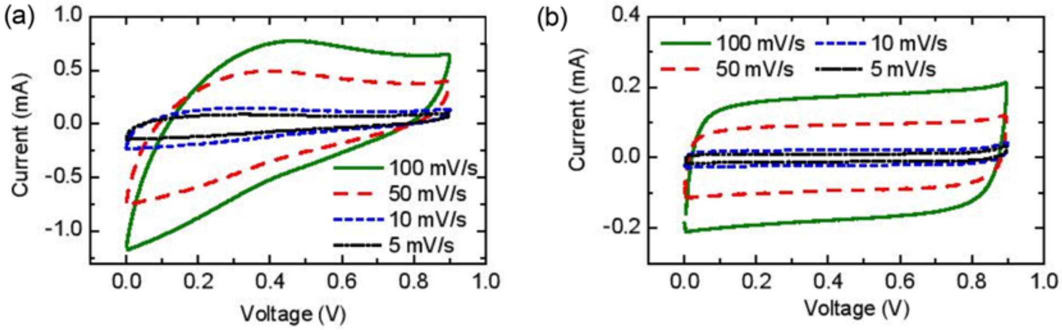

Fig. 9. CV curves of the devices with (a) graphene and (b) CNT electrodes.

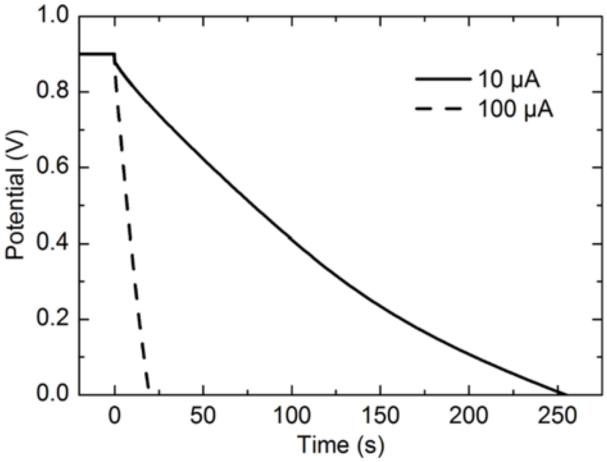

Fig. 10. An example of standard supercapacitor characterization by galvanostatic discharge curves in the case of CNT supercapacitors.

static measurements, and an example curve is shown in Fig. 10. There were no significant differences between the two substrate materials used in the graphene supercapacitors: samples with kaolin-based TP3 had a capacitance of 20 mF, and samples with kaolin-based TP4 17 mF. The specific capacitances were 4.9 and 4.2 F/g, respectively, when accounting only for the active material mass on the electrode overlap area. The difference in specific capacitances may be due to uncertainty in weighing the ink layers: the increase in mass of the substrate due to the ink is very small, resulting in inaccuracy of the determined specific capacitance. Based on these results, kaolin-based substrates worked better as supercapacitors compared to PCC-based substrates, due to greater closed surface and greater suitable porosity.[2]

While the idea of a simple and mass-production-compatible printable supercapacitor is promising, the separator-substrate structure brings some challenges with the encapsulation of the device. Soaking the electrode overlap area in a liquid electrolyte facilitates device characterization under laboratory conditions, but a more robust method is needed for long-term use in an application. As the electrolyte can absorb into the substrate and travel along it, the substrate in the active area needs to be blocked to liquid flow. This could be achieved, for example, by saturating the substrate with a waterproof adhesive. Another way would be to encapsulate the entire freestanding supercapacitor with all the substrate, which then requires a material that does not corrode in aqueous solution. However, the long-term encapsulation was not required in the scope of this work, where the main focus was on the demonstration of the functioning of a proposed novel disposable supercapacitor architecture, which can be fabricated with low cost and high throughput.

4. CONCLUSIONS

We have demonstrated that low-cost pigment-cellulose nanofibril (PCN) composites can be fabricated at pilot scale. Optimization of drying and wet-pressing conditions turned out to be crucial for the generation of smooth and flexible structures. The developed nanoporous PCN composite was successfully used as a double functional separator-substrate in printed supercapacitors. The supercapacitor structure was obtained by simply printing the active layers on both sides of the nanoporous separator-substrate. The graphene and carbon nanotube (CNT)-based inks were used as high surface area active layer materials, and they simultaneously served as current collectors for the supercapacitor. The double functional separator-substrate with kaolin pigments and cellulose nanofibrils (CNF) worked well as an active element in the supercapacitor. The nanoscale porosity of a kaolin-based separator-substrate made it more suitable for printing of active electrodes than a PCC-based substrate. The sheet resistance of the printed graphene layers was lower than that of CNT layers, mostly due to the different coating or printing method. Even though the sheet resistances of graphene and CNT electrodes were different, they resulted in very similar equivalent series resistance (ESR) of the supercapacitors, which suggests that the ESR is mostly caused by the separator-substrate. This type of mass-manufacturing-compatible, low-cost supercapacitor is well suited for energy-harvesting applications and personal devices that require only low currents, and thus do not suffer excessively from high series resistances. Moreover, they can be safely disposed of after use, since they do not contain any toxic materials.

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