Highly Flexible Environmentally Friendly Printed Supercapacitors

T. M. Kraft[1], M. Kujala[1], A. Railanmaa[1], S. Lehtimäki[1], T. Kololuoma[2], J. Keskinen[1], D. Lupo*[1], and M. Mäntysalo[1]
[1]Tampere University of Technology, Faculty of Computing and Electrical Engineering, Tampere, Finland
[2]VTT Technical Research Centre of Finland Ltd., Oulu, Finland
*Corresponding author: donald.lupo@tut.fi, Korkeakoulunkatu 3, 33720, Tampere, Finland

Abstract— In this study, we propose a highly flexible environmentally friendly supercapacitor suitable for low-power Internet-of-Everything applications and the effect of bending (both static and cyclic) on its electrical performance. The supercapacitors are all comprised of carbon electrodes (activated carbon (AC) on a graphite current collector) printed on a flexible plastic substrate, with a NaCl (aq) electrolyte. The capacitance of all the devices is on the order of 0.3 F. Two different substrates (Al coated PET and PP/PA/EVOH/PA/PE [PP-PE]) as well as two different top-bottom substrate sealing methods (heat sealing, adhesive film) were investigated, with the PP-PE substrate and adhesive film sealing found to be preferable. However, all supercapacitors exhibited a rather high tolerance for bending down to a 1.25 cm radius. Little effect on bending reliability was found on the electrode fabrication process (roll-to-roll (R2R) vs. screen printing and manual stencil printing), however R2R printed devices have a higher uniformity of electrical properties. It was confirmed that, if the sealing method is resilient to bending, the degradation of the printed films are not the limiting factor in device flexibility.

I. INTRODUCTION

A vision of the future is that we will be living gadget-free in a hyper-connected Internet-of-Everything (IoE), and that all the tools, information, and services that we require will be at our fingertips. We will be able to live “naked”, *i.e.* free of gadgets and do away with the need for cellphones or other cumbersome devices, while gaining enhanced services related to personal health, security and safety. Key enablers to this visionary IoE network, and possible building blocks of smart surroundings, could be electronic sticker systems called stick-it-on devices (SioDs).[1–3] These devices are defined as flexible, energy autonomous, interactive devices that can perform functions like sensing, actuating, computing, and/or communicating.

The long-term vision of flexible electronics is to have completely printed systems, including interconnects, components and circuits.[4] In general, printed electronics (PE) has provided a means to produce easily manufactured, large area, flexible[5] or stretchable[6] electronic components. Specifically, various solution processing methods have been developed to fabricate displays with light emitting diodes,[7] sensors (i.e. photodetectors, thermistors),[8–10] antennas,[11] energy harvesting (i.e. photovoltaics),[12] energy storage (i.e. batteries and supercapacitors),[13-17] and even integrated circuits printed in small volumes.[18] Of particular value for this *trillion sensor network* is the use of recyclable printed energy storage units (i.e. supercapacitors with carbon electrodes and salt water electrolyte) which could help increase the sustainability of energy autonomous SioDs.

Supercapacitors are electrochemical components that are able to provide higher specific power compared with batteries (with lower specific energy).[19,20] A supercapacitor may consist of two electrodes separated by an ionically conductive electrolyte. The electrolyte is absorbed by the porous electrodes, between which a permeable separator is located. The electrodes are typically made of activated carbon (AC) powder that is bound using fluorine containing polymers such as polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF).

Existing competing solutions for printed electrochemical energy storage include various types of thin-film batteries, fuel cells, and supercapacitors.[21] However, due to the increased cycle life and lack of toxic, corrosive or strategically critical materials, supercapacitors are a promising energy storage component of remote energy autonomous systems. The approach taken herein with printed carbon electrodes on flexible plastic substrates involves low fabrication temperatures (below 150 °C) which in turn not only increases the potential substrate use but also decreases the overall fabrication cost.[22] Furthermore, the use of non-toxic materials makes these supercapacitors an attractive option for applications in ubiquitous energy autonomous nodes.

Recently, it has been shown that supercapacitors can be applied as energy storage components with sensors and in autonomous sensor networks,[23] as well as in active RFID tags,[24] wearable, health and sports applications.[25] In these applications supercapacitors can store the required energy obtained from primary energy sources such as photovoltaic cells or RF harvesters.[26,27] Furthermore, supercapacitors are also able to provide higher peak power than the primary energy sources (i.e. OPVs under ambient lighting). In many of these applications, the supercapacitor can be a part of a recyclable or disposable device, so it is preferred that the device is manufactured with environmentally friendly materials and be either biodegradable or incinerable. Moreover, the materials and fabrication costs should be low. As these demands are hard to fulfill with the conventional battery or supercapacitor technology there clearly is a need for novel supercapacitor materials and fabrication methods.

Organic based electrolytes utilizing solvents such as propylene carbonate or acetonitrile are commonly used, but it is also possible to use aqueous based electrolytes, and naturally derived AC binders (e.g. chitosan). With water based electrolytes the maximum voltage is limited to approximately 1.23 V,[28] whereas with organic electrolytes a voltage of approximately 2.5 V can be applied between the electrodes.[29]

As well as being made from environmentally friendly materials and by means of printed fabrication processes, an attractive aspect of the supercapacitors used in this study is their mechanical flexibility.[30] Flexible electronics has evolved significantly from flexible circuits, in which only the wiring was printed onto flexible substrates, to flexible components. Furthermore, with the incorporation of graphite current collectors a great deal of flexibility is achieved, with future prospective research leading to stretchable devices.[31] The ease in which the supercapacitors can be incorporated into various applications, be it wearables or nearables (electronics embedded in the surroundings), is enhanced by their inherent flexibility. [32–35] Furthermore, unlike previous studies, these supercapacitors have an architecture that is elegantly simplistic, using low cost materials, and roll-to-roll (R2R) screen printing.

With the physical flexibility of energy autonomous sticker-like systems and printed components becoming increasingly more relevant, we have investigated the performance of the devices under bending stress. Our study compares the impact of substrate material and adhesive on the supercapacitors' performance reliability.

II. EXPERIMENTAL

The supercapacitor architecture is shown in Figure 1. The devices comprise a thin polymer substrate, graphite and activated carbon inks and neutral aqueous electrolyte. Two different substrates, two different sealing methods (heat sealing and adhesive film) and two different printing methods (R2R, stencil) were compared to each other in the measurements. The substrates consisted of either aluminum coated polyethylene terephthalate (AL/PET) or multilayered laminate packaging film (PP/PA/EVOH/PA/PE a.k.a PP-PE).

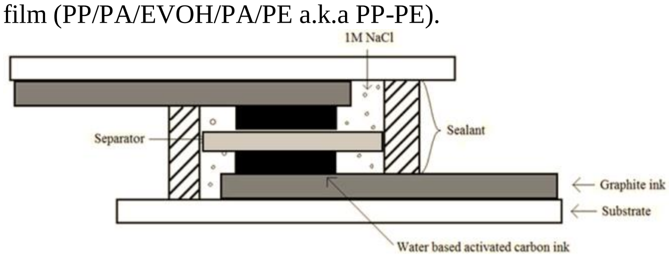

Figure 1. Supercapacitor architecture.

Ten supercapacitors were made per architecture and eight of them were subjected to static and cyclic bending tests; with two as references (to separate the effects of charge-discharge cycling from those of bending). In the static bending measurement, supercapacitors were first characterized using a Maccor 4300 (Maccor Inc., USA), then bent for 12 h prior to re-measurement. 5 cm, 3.5 cm and 2.5 cm cylinder diameters were used. During the static bending study, each supercapacitor went through the measurement program 5 times: pre-bending, bent at; 5 cm, 3.5 cm, and 2.5 cm, and post-bending.

In the cyclic bending stress measurement, supercapacitors were attached between two plates whose vertical motion was controlled by an Instron 4411 Universal Tensile Machine (UTM). Plate distances varied from 4.5 cm to 1.5 cm and 4 cm to 1.5 cm for bending, depending on the bending axis. The speed of the plates was in both cases 500 mm/min and the plates were cycled 500 times.

B. Device Fabrication: The laminate Al/PET was supplied from Walki Oy with 9 µm Al foil on 50 µm PET film. The composite packaging film from Wipak Oy has thickness of 146 µm with a PP/PA/EVOH/PA/PE structure.

Stencil printed electrodes and current collectors were prepared in the laboratory using 120 µm stainless steel stencils. Current collectors (20 mm x 30 mm) were printed using Henkel Electrodag PF407C graphite ink. The ink was dried in a forced convection oven at 120 °C for 15 min when printed on the Al-PET substrate and at 90 °C for 22 min for the composite packaging film. After drying the graphite ink an activated carbon (AC) electrode (10 mm x 18 mm) was printed on a portion of the graphite. The AC ink was allowed to dry in ambient air for 1hr minimum. The AC ink was formulated as described in an earlier publication[13]. A stylus profilometer (Bruker DektakXT) was used to determine the cured carbon ink thickness.

Roll-to-roll (R2R) printed electrodes were performed at VTT Technical Research Centre of Finland. VTT's ROKO facility, equipped with Gallus rotary-screen printing units was used. All layers were printed using the Gallus BY screens. The mesh count for this type of screen is 64 Meshes per inch, open screen area of 56 %, and the plate thickness of 210 µm. Henkel Electrodag PF407C graphite ink was used for the current collector printing. A self-made activated carbon ink, made according the recipe given above and three-roll-milled twice, with a Marabu VP retarder, 11 wt.%, was used. Printing speed for all samples was 2 m/min. For the current collectors printed on the Wipak composite packaging film N2/Ar plasma-treatment with corresponding gas pressures of 5/6 bar was utilized to enhance the current collector adhesion on the laminate. With Al-PET substrate the plasma treatment even with the smallest possible plasma power causes the warpage of the substrate and was therefore not used. Most likely Al is conducting heat generated during the plasma treatment effectively on the PET substrate causing it to warp. The other difference between the laminated packaging film and Al-PET film is the temperature used for the curing. For the Al-PET the ovens, 4 x 1 m, were heated to 120 °C whereas the Wipak composite film was cured at 90 °C. For the activated carbon the ovens were set to 90 °C for both type of films to get comparable thermal history between the samples. A stylus profilometer (Bruker DektakXT) was used to determine the cured carbon ink thickness.

Device fabrication following electrode printing. Substrates were cut into 4 cm x 4 cm pieces and the supercapacitors were assembled in Tampere University of Technology (TUT). Two electrodes faced each other and sealed together so that between the two electrodes they have a separator paper (Dreamweaver Silver AR40, 16mm x 23mm) and excess electrolytic solution (1 M NaCl) (NaCl ≥ 99.8 %, Sigma-Aldrich). As previously mentioned, two different sealing methods (3M adhesive and heat seal). The adhesive (3M 200MP/468MP) was applied on the substrate at room temperature and did not involve additional processing steps. The heat sealing method for Al/PET was combined with a hot melt sealant (Paramelt Aquaseal X2277) which was applied to the edges of the substrate and over the current collector and annealed at 80 °C for 15 min prior to heating with an impulse heat sealer. Whereas, with PP-PE the hot melt sealant was only applied over the current collector as the two PE layers fuse together when heated and pressed. The additional adhesive on top of the current collector was used to provide improved adhesion on the interface between the graphite and the substrate.

*B. Electrical Characterization of Supercapacitors***:** A Maccor 4300 (Maccor Inc., USA) testing apparatus was used for all electrical characterizations. In each Maccor measurement a sample was charged and discharged to 0.9 V at 1 mA three times, then charged to 0.9 V and the voltage held for 30 minutes. After this, the sample was discharged at 1 mA, charged to 0.9 V, held there for 1 hour and then discharged. At the end the sample was charged and discharged to 0.9 V at 3 mA and at 10 mA, three cycles each.

III. RESULTS AND DISCUSSION

A. Characterization results

In the initial characterization, the stencil printed devices demonstrate significantly higher spread in capacitance and ESR values than the R2R printed devices. This not surprising since stencil printing a manual printing method more subject to process deviation. The gathered results are shown in Table 1. It should be noted that the performance requirements in terms of capacitance and ESR are quite different for supercapacitors in a low power wireless sensor than for common applications such as electric vehicles.

Table 1. Summary of supercapacitors' electrical characteristics.

Electrode Printing Method	*Substrate*	*Sealing Method*	*capacitance (mF) min – max (mean; StdDev)*	*ESR (Ω) min – max (mean; StdDev)*	*leakage current (μA) min – max (mean; StdDev)*
R2R	Al/PET	Adhesive Film	243 – 276 (**260**; 9)	21 – 29 (**25**; 3)	8 – 10 (**9**; 0.4)
R2R	Al/PET	Heat Seal	224 – 275 (**244**; 17)	29 – 37 (**33**; 3)	6 – 9 (**7**; 0.8)
R2R	PP-PE	Adhesive Film	228 – 235 (**230**; 2)	28 – 34 (**31**; 2)	8 – 9 (**9**; 0.3)
R2R	PP-PE	Heat Seal	222 – 239 (**227**; 5)	37 – 55 (**47**; 6)	10 – 11 (**10**; 0.6)
Stencil	Al/PET	Adhesive Film	322 – 465 (**373**; 45)	17 – 37 (**23**; 6)	7 – 11 (**8**; 1.5)
Stencil	Al/PET	Heat Seal	255 – 553 (**384**; 79)	18 – 56 (**32**; 12)	5 – 10 (**7**; 1.5)
Stencil	PP-PE	Adhesive Film	219 – 519 (**353**; 77)	27 – 58 (**41**; 9)	6 – 11 (**9**; 1.4)
Stencil	PP-PE	Heat Seal	218 – 583 (**393**; 97)	31 – 62 (**44**; 11)	7 – 16 (**10**; 2.5)

B. Static bending results

Supercapacitors were electrically characterized and then bent for at least 12 hours along the substrate axis. Following the bending characterization, the devices were measured while flat (also held for 12 hours) and weighed to ensure the electrolyte had not evaporated. As a voltage hold of 1.5 h was included in one measurement, it is important to account for aging effects, which occur more quickly with a voltage hold than with charge-discharge cycling.[36] However, it is particularly relevant to note the prolonged resilience of the devices to bending. For most of the PP-PE adhesively sealed supercapacitors' the charge and discharge cycles were identical before and after bending.

Table 2. Mean breakdown averages (of all three electrical parameters) for static bending of supercapacitors from 5 cm to 2.5 cm.

Sealing Method	*Substrate*		
	Al/PET	PP-PE	Overall
Heat Seal	77.1 %	10.4 %	**43.8 %**
Adhesive Film	2.1 %	2.1 %	**2.1 %**
Overall	**39.6 %**	**6.3 %**	

The electrical characteristics of the devices throughout the bending process were monitored and provide evidence of breakdown as the devices were bent from 5 cm to 2.5 cm diameters (population failures summarized in Table 2).

It is evident that the 3M adhesive seal and PP-PE substrate survive bending most effectively, with the heat sealed devices most prone to failure.

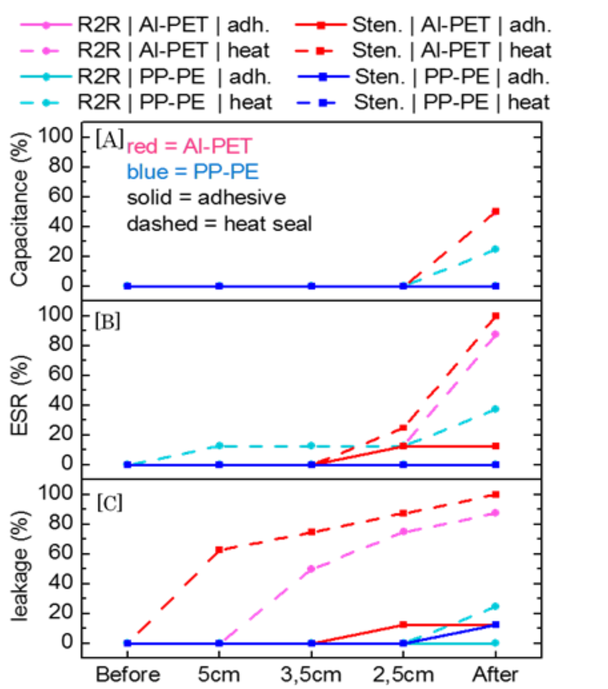

Figure 5*: Device failure rate in terms of [A] capacitance, [B] equivalent series resistance (ESR), and [C]leakage current as bending diameter is decreased.* ***Printing method****: roll-to-roll = R2R; stencil = Sten;* ***Substrates****: Al-PET = aluminum coated PET; PP-PE = PP/PA/EVOH/PA/PE.* ***Sealing method****: adhesive = 3M adhesive; heat seal = heat sealing method.*

Figure 5A, 5B, and 5C, monitor the population breakdown for the devices' capacitance, equivalent series resistance (ESR), and leakage current respectively. The device failure percentage in terms of capacitance is shown in

A with a breakdown limit set to -10%. This implies that if there is 10% drop in capacitance from measurements before to after bending, then the device is considered to have failed. Even though the capacitance does not show as much variation in the breakdown it is evident that the adhesive seal and PP-PE substrate survive bending most effectively, with the heat sealed devices most prone to failure. For the analysis of the ESR failure limits, the threshold was set to a 50% increase; the results are summarized in Figure 5B. Similarly to the capacitance results, the adhesive sealing method and PP-PE substrate devices have the highest resilience to bending. Furthermore, this trend continues with the leakage current degradation seen in 5C. The breakdown in this case was defined as any increase in the leakage current, as the leakage current in the reference samples decreased during the measurement cycling. In samples where the sealing breaks, additional oxygen is introduced in the device, which increases the leakage current significantly. In samples where the sealing stayed intact during bending, the leakage current decreased gradually in the same way as in the reference samples.

For the heat sealing method it was found that Al/PET substrates exhibited the highest number of failed devices. However, even though a hot melt sealant was used for the Al/PET substrates it is not as effective as the PE-PE heat seal when using the PP-PE multi-layer film. Nevertheless, the adhesive film shows the highest resilience to bending fatigue.

C. Cyclic bending results

After the static bending tests, the R2R printed samples were subjected to cyclic bending. Two different bending axes were used: stress along the graphite layer or stress along the substrate. The breakdown results after 500 bending cycles are shown in Table 3. The same breakdown criteria were used as in the static bending measurements.

Clearly, the cyclic bending has very little effect on the electrical performance of the supercapacitors. However, in this study the Al/PET has a slightly higher survival rate than the PP-PE. The difference is explained by the change in leakage current, which is normally associated with increased oxygen uptake in the device's electrolyte through the substrate.[37]

Table 3. Mean population failures for cyclic bending of supercapacitors from 4,5cm or 4 cm to 1,5cm, sealed with adhesive film.

Orientation	*Substrate* Al/PET	PP-PE
Substrate stress	0 %	4.17 %
Graphite stress	0 %	16.67 %

IV. Conclusion

This study provides clear evidence that the printed supercapacitors with NaCl (aq) electrolyte are highly flexible and resilient to bending stress. With the analysis of devices' capacitance, ESR, and leakage current it was possible to monitor device performance as bending stress was applied (both statically and dynamically). The failure mechanism was attributed to the seal between the top and bottom substrates, which failed and created ambient air exposure to the electrolyte. Furthermore, it was shown that if the sealing method is resilient to bending, the current collector and AC electrodes are not the limiting factors to bending stress failures. As seen in Table 2 (overall static bending failures) and Table 3 (overall fatigue bending stress failures) the printed supercapacitors are highly resilient to bending. These results show a clear example of highly flexible (bending down to 1.25 cm radius), environmentally friendly, supercapacitors having promise for energy autonomous flexible electronic systems.

Acknowledgment

This work was partially funded by Business Finland as a part of the Naked Approach project [decision #40337/14 (TUT) and 3131/31/2014 (VTT)] and the Towards Digital Paradise project (decision no. 2742/31/2016). M. Mäntysalo is supported by Academy of Finland (grant no. 288945 and 294119) and T. Kraft is thankful for his postdoctoral research fellowship received from the Tampere University of Technology Foundation.

References

1.Naked Approach | Nordic perspective to gadget-free hyperconnected environments. Available at: http://nakedapproach.fi/. (Accessed: 18th August 2017)
2.Kraft, T. M. *et al.* High density R2R screen printed silver interconnections for hybrid system integration. in *2016 6th Electronic System-Integration Technology Conference (ESTC)* 1–6 (2016). doi:10.1109/ESTC.2016.7764477
3.Mantysalo, M. & Kraft, T. M. Integrating Printed and Silicon Electronics. in (2016).
4.*OE-A Roadmap for Organic and Printed Electronics - 7th Edition*. (OE-A, 2017).
5.Koskinen, S., Pykari, L. & Mantysalo, M. Electrical Performance Characterization of an Inkjet-Printed Flexible Circuit in a Mobile Application. *IEEE Trans. Compon. Packag. Manuf. Technol.* **3,** 1604–1610 (2013).
6.Suikkola, J. *et al.* Screen-Printing Fabrication and Characterization of Stretchable Electronics. *Sci. Rep.* **6,** (2016).
7.Halls, J. Ink-Jet printing of PLED displays. *Inf. Disp.* **2,** 11 (2005).
8.Rim, Y. S., Bae, S.-H., Chen, H., De Marco, N. & Yang, Y. Recent Progress in Materials and Devices toward Printable and Flexible Sensors. *Adv. Mater.* **28,** 4415–4440 (2016).
9.Vuorinen, T., Niittynen, J., Kankkunen, T., Kraft, T. M. & Mäntysalo, M. Inkjet-Printed Graphene/PEDOT:PSS Temperature Sensors on a Skin-Conformable Polyurethane Substrate. *Sci. Rep.* **6,** 35289 (2016).
10.Cui, Z. *et al.* Design and operation of silver nanowire based flexible and stretchable touch sensors. *J. Mater. Res.* **30,** 79–85 (2015).
11.Parrish, P. T. *et al.* Printed Dipole-Schottky Diode Millimeter Wave Antenna Array. in **0337,** 49–52 (1982).
12.El Hajj, A. *et al.* Flexible inverted polymer solar cells with an indium-free tri-layer cathode. *J. Appl. Phys.* **115,** 033103 (2014).
13.Keskinen, J. *et al.* Architectural modifications for flexible supercapacitor performance optimization. *Electron. Mater. Lett.* 1–9 (2016). doi:10.1007/s13391-016-6141-y
14.Bae, J. *et al.* Fiber Supercapacitors Made of Nanowire-Fiber Hybrid Structures for Wearable/Flexible Energy Storage. *Angew. Chem. Int. Ed.* **50,** 1683–1687 (2011).
15.Lehtimäki, S. *et al.* Low-cost, solution processable carbon nanotube supercapacitors and their characterization. *Appl. Phys. A* **117,** 1329–1334 (2014).
16.Yang, Z., Deng, J., Chen, X., Ren, J. & Peng, H. A Highly Stretchable, Fiber-Shaped Supercapacitor. *Angew. Chem. Int. Ed.* **52,** 13453–13457 (2013).
17.Lee, Y.-H. *et al.* Wearable Textile Battery Rechargeable by Solar Energy. *Nano Lett.* **13,** 5753–5761 (2013).
18.Ha, M. *et al.* Printed, Sub-3V Digital Circuits on Plastic from Aqueous Carbon Nanotube Inks. *ACS Nano* **4,** 4388–4395 (2010).
19.Supercapacitors, E. *Scientific Fundamentals and Technological Applications, ed. BE Conway*. (Plenum Publishing Co., New York, 1999).
20.Beguin, F. & Frackowiak, E. *Supercapacitors: Materials, Systems and Applications*. (John Wiley & Sons, 2013).
21.Winter, M. & Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? *Chem. Rev.* **104,** 4245–4270 (2004).
22.Koo, M. *et al.* Bendable Inorganic Thin-Film Battery for Fully Flexible Electronic Systems. *Nano Lett.* **12,** 4810–4816 (2012).
23.Liu, Z., Yang, X., Yang, S. & McCann, J. Efficiency-Aware: Maximizing Energy Utilization for Sensor Nodes Using Photovoltaic-Supercapacitor Energy Systems. *Int. J. Distrib. Sens. Netw.* **9,** 627963 (2013).
24.Shoemaker, J. The Real World of Active RFID Tags. *RFID J.* **2014,** 1–3
25.Stoppa, M. & Chiolerio, A. Wearable Electronics and Smart Textiles: A Critical Review. *Sensors* **14,** 11957–11992 (2014).
26.Lehtimäki, S. *et al.* Performance of printable supercapacitors in an RF energy harvesting circuit. *Int. J. Electr. Power Energy Syst.* **58,** 42–46 (2014).
27.Tuukkanen, S., Välimäki, M., Lehtimäki, S., Vuorinen, T. & Lupo, D. Behaviour of one-step spray-coated carbon nanotube supercapacitor in ambient light harvester circuit with printed organic solar cell and electrochromic display. *Sci. Rep.* **6,** (2016).
28.Millet, P. Fundamentals of Water Electrolysis. in *Hydrogen Production* (ed. Godula-Jopek, A.) 33–62 (Wiley-VCH Verlag GmbH & Co. KGaA, 2015). doi:10.1002/9783527676507.ch2
29.Balducci, A. *et al.* High temperature carbon–carbon supercapacitor using ionic liquid as electrolyte. *J. Power Sources* **165,** 922–927 (2007).
30.Kim, B. C., Hong, J.-Y., Wallace, G. G. & Park, H. S. Recent Progress in Flexible Electrochemical Capacitors: Electrode Materials, Device Configuration, and Functions. *Adv. Energy Mater.* **5,** (2015).
31.Kim, T. *et al.* Inkjet-printed stretchable single-walled carbon nanotube electrodes with excellent mechanical properties. *Appl. Phys. Lett.* **104,** 113103 (2014).
32.Xu, Y. *et al.* Flexible Solid-State Supercapacitors Based on Three-Dimensional Graphene Hydrogel Films. *ACS Nano* **7,** 4042–4049 (2013).
33.Meng, C., Liu, C., Chen, L., Hu, C. & Fan, S. Highly Flexible and All-Solid-State Paperlike Polymer Supercapacitors. *Nano Lett.* **10,** 4025–4031 (2010).
34.Chen, P., Chen, H., Qiu, J. & Zhou, C. Inkjet printing of single-walled carbon nanotube/RuO2 nanowire supercapacitors on cloth fabrics and flexible substrates. *Nano Res.* **3,** 594–603 (2010).
35.Jost, K. *et al.* Knitted and screen printed carbon-fiber supercapacitors for applications in wearable electronics. *Energy Environ. Sci.* **6,** 2698–2705 (2013).
36.Weingarth, D., Foelske-Schmitz, A. & Kötz, R. Cycle versus voltage hold – Which is the better stability test for electrochemical double layer capacitors? *J. Power Sources* **225,** 84–88 (2013).
37.Lehtimäki, S. *et al.* Performance, stability and operation voltage optimization of screen-printed aqueous supercapacitors. *Sci. Rep.* **7,** (2017).