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Screen Printing Technology for Energy Devices

Andreas Willfahrt

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by

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Dedicated to my family,
my three gorgeous girls.

Abstract

The technical application of screen and stencil printing has been state of the art for decades. As part of the subtractive production process of printed circuit boards, for instance, screen and stencil printing play an important role. With the end of the 20th century, another field has opened up with organic electronics. Since then, more and more functional layers have been produced using printing methods. Printed electronics devices offer properties that give almost every freedom to the creativity of product development. Flexibility, low weight, use of non-toxic materials, simple disposal and an enormous number of units due to the production process are some of the prominent keywords associated with this field.

Screen printing is a widely-used process in printed electronics, as this process is very flexible with regard to the materials that can be used. In addition, a minimum resolution of approximately 30 μm is sufficiently high. The ink film thickness, which can be controlled over a wide range, is an extremely important advantage of the process. Depending on the viscosity, layer thicknesses of several hundred nanometres up to several hundred micrometres can be realised.

The conversion and storage of energy is an important topic, either in the field of renewable energies or the energy supply of the Internet of Things (IoT). This thesis addresses the print production of both device classes. Vertically structured thermoelectric generators (TEGs) for energy conversion and stacked supercapacitors for energy storage are produced by screen printing.

Papers I-IV focus on the generation of functional layers of vertically aligned thermoelectric generators. These can convert heat directly into electrical energy. The vertical design was chosen due to the simple application of the device at the heat source. The general feasibility of screen-printed, vertically aligned TEGs was demonstrated. Optimisation of the thermoelectric materials is required, so that the process can be used sensibly. In **paper III**, the Ni containing model ink was optimised for filling the cavities in the insulator layer. In **paper IV** the printed thermoelectric generators are modelled. The performance of a set of parameters can be estimated by this model. The high Seebeck coefficient of ionic conductors is used in **paper V** in so-called ionic thermoelectric supercapacitor (ITESC), a combination of TEG and supercapacitor. **Paper VI** presents an environmentally friendly supercapacitor with a printable separator based on cornstarch and citric acid, which has a competitive electrochemical performance compared to printed supercapacitors reported elsewhere. In **paper VII**, some parameters of screen-printed primary Zn/MnO₂ cells are optimised and a printable separator based on cornstarch and lactic acid was successfully tested.

Populärvetenskaplig sammanfattning

Den tekniska tillämpningen av skärm- och stencilutskrift har varit topp-moderna i årtionden. Som en del av den subtraktiva produktionsprocessen av tryckta kretskort spelar exempelvis skärm- och stencilutskrift en viktig roll. I slutet av 1900-talet har ett annat fält öppnat med organisk elektronik. Sedan dess har allt fler funktionella lager producerats med hjälp av tryckmetoder. Tryckta elektronikanordningar erbjuder egenskaper som ger nästan all frihet till kreativiteten i produktutvecklingen. Flexibilitet, låg vikt, användning av giftfria material, enkelt bortskaffande och ett enormt antal enheter på grund av produktionsprocessen är några av de framträdande nyckelord som hör till detta område.

Skärmtryck är en allmänt använd process i tryckt elektronik, eftersom processen är mycket flexibel med avseende på material som kan användas. Dessutom är en minsta upplösning på cirka 30 μm tillräckligt bra. Bläckfilmens tjocklek, som kan styras över ett brett område, är en extremt viktig fördel med processen. Beroende på viskositeten kan skiktjockleken på flera hundra nanometer upp till flera hundra mikrometer realiseras.

Omvandling och lagring av energi är ett viktigt ämne, antingen inom förnybara energikällor eller energiförsörjningen av saker i saken (IoT). Denna avhandling riktar sig till utskriftsproduktionen av båda enhetsklasserna. Vertikalt strukturerade termoelektriska generatorer (TEG) för energiomvandling och staplade superkapacitorer för energilagring produceras genom skärmutskrift.

Publikationer I-IV fokuserar på generering av funktionella lager av vertikalt inriktade termoelektriska generatorer. Dessa kan omvandla värme direkt till elektrisk energi. Den vertikala konstruktionen valdes på grund av enkel anordning av anordningen vid värmekällan. Det generella genomförbara av skärmtryckta vertikalt anpassade TEG-skivor visades. Optimering av termoelektriska material krävs, så att processen kan användas förnuftigt. I **publikation III** optimerades den Ni-innehållande modellfärgen för fyllning av kaviteterna i isolatskiktet. I **publikation IV** modelleras de tryckta termoelektriska generatorerna. Utförandet av en uppsättning parametrar kan beräknas med denna modell. Den höga Seebeck-koefficienten för jonledare används i **publikation V** i så kallad jonisk termoelektrisk superkapacitor (ITESC), en kombination av TEG och superkapacitor. **Publikation VI** presenterar en miljövänlig superkapacitet med en utskrivbar separator baserad på majsstärkelse och citronsyra, som har en konkurrenskraftig elektrokemisk prestanda jämfört med tryckta superkapacitorer som rapporterats någon annanstans. I **publikation VII** optimeras vissa parametrar av skärmtryckta primära Zn/MnO_2 -celler och en testbar separator baserad på majsstärkelse och mjölksyra testades med framgång.

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“The journey is the reward”

Confucius

comes closest to german aphorism “Der Weg ist das Ziel”. This sentence best describes how I feel about my doctoral thesis, which is now being completed. The journey was longer than I initially thought, but with the proverb in mind I was more blessed than ‘condemned’ by this long journey.

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“It does not matter how slowly you go as long as you do not stop.”

Confucius

Stuttgart/Norrköping, February 2019

Andreas Willfahrt

Publications included in the Thesis

Paper I:

Optimising Stencil Thickness and Ink Film Deposit

Andreas Willfahrt, John Stephens, Gunter Hübner

International Circular of Graphic Education and Research, 4, pp.6-17, 2011

Contribution: All the conceptual and most of the experimental work.

Wrote the first draft and was involved in the final editing of the paper.

Paper II:

Optimization of aperture size and distance in the insulating mask of a five layer vertical stack forming a fully printed thermoelectric generator

Andreas Willfahrt, Gunter Hübner

Advances in Printing and Media Technology, Vol. 38, pp. 261–269, 2011

Contribution: All the conceptual and most of the experimental work.

Wrote the manuscript and did the final editing of the paper.

Paper III:

Screen printing into cavities of a thick insulating layer as a part of a fully printed thermoelectric generator

Andreas Willfahrt, Jochen Witte, Gunter Hübner

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Paper IV:

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Andreas Willfahrt, Erich Steiner

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Contribution: Involved in development of the theory. Wrote the first draft and was involved in the final editing of the paper.

I would like to thank the IARIGAI and the International Circle for the permission to use the publications I-IV in this thesis.

Paper V:

Tunable ionic thermoelectrics for ultra-sensitive, large-area printed thermopiles
Dan Zhao, Anna Martinelli, Andreas Willfahrt, Thomas Fischer, Diana Bernin, Zia Ullah Khan, Maryam Shahi, Joseph Brill, Magnus P. Jonsson, Simone Fabiano, Xavier Crispin

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Contribution: Experimental work in printing of ionic thermoelectrics

Paper VI:

Screen-Printable Acid Modified Cornstarch as Non-Toxic,
Disposable Hydrogel-Polymer Electrolyte in Supercapacitors
Andreas Willfahrt, Erich Steiner, Jonas Hötzel, Xavier Crispin
Submitted to Flexible and Printed Electronics; review in progress

Contribution: All conceptual and most experimental work. Wrote the manuscript and final editing of the paper.

Paper VII:

Parameter Evaluation of Printed Primary Zn / MnO₂-Batteries with Nonwoven and Hydrogel Separator
Andreas Willfahrt, Thomas Fischer, Serhat Sahakalkan, Michael Krebs, Erich Steiner
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Contribution: Concept of the paper. Most part of the experimental and theoretical work. Wrote the manuscript, and final editing of the paper.

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Paper VIII:

Screen printed thermoelectric generator in a five layers vertical setup
Andreas Willfahrt, Gunter Hübner, Erich Steiner, Xavier Crispin
Proceeding of Large-Area, Organic and Polymer Electronics Convention 2011 (LOPE-C 11), pp. 196 – 200, 2011

Paper IX:

Improving the electrical performance and mechanical properties of conductive ink on thin compound substrate
Andreas Willfahrt, Thomas Fischer, Gunter Hübner
J. Print Media Technol. Res., Vol. 5, No. 1, pp.7-14, 2016

Abbreviations and Symbols

AC	activated carbon
ATR	attenuated total reflection
CA	citric acid
CE	counter electrode
CPE	composite polymer electrolyte
CV	cyclic voltammetry
DSA	drop shape analysis
EDLC	electric double layer capacitors
EDL	electric double layer
EIS	electrochemical impedance spectroscopy
EOM	emulsion over mesh
ESR	equivalent series resistance
FET	field effect transistor
FTIR	fourier-transform infrared spectroscopy
GCD	galvanostatic charge/discharge cycling
GEIS	EIS performed under galvanostatic control
GPE	gel polymer electrolyte
IHP	inner Helmholtz plane
IL	ionic liquid
IoE	internet of everything
IoT	internet of things
IRdrop	voltage drop
ITESC	ionic thermoelectric supercapacitor
LAOS	large amplitude oscillatory shear
LVR	linear viscoelastic region
OHP	outer Helmholtz plane
OWRK	Owens, Wendt, Rabel and Kaelble
PEIS	EIS performed under potentiostatic control
PCB	printed circuit boards
RE	reference electrode
SAOS	small amplitude oscillatory shear
SPE	solid polymer electrolyte
TE	thermoelectric
TC	thermocouple
TEC	thermoelectric cooler
TEG	thermoelectric generator
WE	working electrode

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Part I

Background

1 Introduction

1.1 Printed & Organic Electronics

The Nobel Prize in Chemistry awarded to Heeger, MacDiarmid and Shirakawa in the year 2000 ^[1] represents a distinctive landmark in the evolution of functional printing. Printed Circuit Boards (PCB) have been around for several decades ^[2] and also membrane keyboards, which were patented in the 1970s were widely-used. But with the discovery of conductive polymers in 1977, the applications of functional printing have significantly increased. It took 20 years from the discovery of conductive polymers until the first fully printed transistor was reported, see Figure 1. But the enthusiasm for soluble conductive polymers was stimulated by the idea that this class of materials could be used as an ink in low-cost and well established printing processes. With the new millennium, interest in research in the field of printed electronics grew and the first fully screen printed organic field effect transistor (OFET) was demonstrated ^[6].

From then on, organic and printed electronics (PE) started a common path with the aim of being able to manufacture certain applications and devices using ubiquitously available processes at low investment costs. Very high quantities and low unit costs are thus possible, which enables mass application of the products manufactured in this way.

Many ideas and concepts are springing up from the breeding ground of scientific laboratories and research institutes, so that the already industrialised and established print production of aforementioned devices appears more or less unspectacular. For roughly 20 years now, printed electronics has been experiencing one innovation after another. Recently, flexible and stretchable electronic devices, which can be mounted in textiles or directly on the body, have also become of interest. The Horizon 2020 call „Flexible and Wearable Electronics“

Figure 1. 30 years of printed and organic electronics ^[1, 4-6].

with a total budget of 30 million Euros shows the attractiveness of this field of research. Current publications contain interesting work in this field. Among others, a breathable, skin-friendly blood leakage sensor was presented ^[7], a flexible graphene-based supercapacitor printed on cotton textile ^[8] was demonstrated, and screen printed electrodes for electrocardiography (ECG) application with improved spatial resolution ^[9] have been reported.

In addition to the constantly evolving new approaches, there are mature concepts and devices that have already proven themselves, some of which are already mass products ^[10] or are aiming for the next step towards mass application. The principal feasibility of printed components as antennas, sensors, actors, energy sources and harvesters have already been shown. But many observers of this branch of technology are still waiting for the one, big killer application, which ultimately paves the way for printed electronics as a key technology. Whether this application will ever come, or whether printed electronics should be seen as a niche technology rather than a disruptive one, that will show the future. Printed electronics has already come a long way towards a technology that has been taken seriously beyond the successes in the laboratory. When talking to representatives from the industries, the topic of printed electronics is always of interest, but established processes and possibly certified products are difficult to replace. Again, hope is set on the killer application which may lead to a drastic reduction of costs. The research work must therefore not only be carried out on individual devices, but must also be directed towards an entire system that makes it easy for decision-makers to try to implement the new technology.

One of the topics that can be addressed by printed electronics is the Internet of Things (IoT), which is a combination of components with different hardware and software characteristics. IoT is a long-standing but still growing megatrend, which is being further promoted by the growing digitisation of society as a whole. The advanced Internet of Everything (IoE) does not only connect intelligent things but also processes and data ^[11], creating an all-embracing network that can be used to monitor and automate tasks.

IoT requires appropriate sensors including power sources, which can transmit their data at regular intervals. The autonomy of the sensors is important, as they can also be used in places where there is no access to the power grid. Energy harvesting can be the solution to this problem in order to operate such sensor nodes. However, many energy harvesters only supply energy intermittently or are subject to unforeseeable fluctuations that must be compensated for by appropriate energy storage systems. Further, some energy harvesters simply do not deliver enough energy ^[12]. Therefore the combination of energy harvesting and energy storage devices is crucial. If it is possible to use printing technology to manufacture these devices, it is very likely that low-cost, high-volume and at best environmentally friendly autonomous sensors will be

produced that can perform special tasks in our daily lives as part of the Internet of Everything.

This work addresses both the areas of energy harvesting and energy storage. The realisation of the components by means of printing technology is a common factor. The generation of multilayer printing layers with similar functional printing pastes is another.

1.2 Aim and Outline of the Thesis

This thesis addresses components of printed electronics that are suitable for the power supply of IoT devices, more especially thermoelectric modules for converting heat into electricity and supercapacitors/batteries for storing electrical energy.

A thermoelectric module is composed of the replication of vertical thermocouples made of n-type and p-type legs. These legs are made of organic/inorganic semiconductors in the case of thermoelectric generators and polymer electrolytes in the case of thermoelectric supercapacitors or ionic thermopiles. The material is sandwiched between bottom and top metal electrodes. Thermoelectric devices are based on the generation of an electric potential difference between the top and bottom of the thermoelectric legs. The voltage produced is proportional to the temperature difference, which is directly related to the length of the legs, i.e. the thickness of the printed patterns. A decent thermoelectric voltage is achieved when the thermoelectric legs are at least 10-100 μm long and 10-100 thermocouples are electrically connected to form a thermoelectric module. Micro-thermoelectric modules of this thickness can be subjected to temperature differences of up to 30 K during active cooling / heating, thus generating a thermoelectric voltage of 1 V.

The half structure of a battery or a supercapacitor is composed of a metal current collector, an electrode layer (typically a mixed electron-ion conductor) and an electrolyte, as shown in Figure 2. The aim is to store as much charge as possible, which is – depending on the application – related to the mass or volume of the electrodes. Since charge is solely stored in the electrode material, the mass of the current collector and the electrolyte is basically ‘dead’. It is therefore desirable to have a reasonably thick layer of electrode material and a thin layer of current collector and electrolyte material.

This brief description shows that these energy devices require the ability to produce layers and patterns with a thickness of about 10-100 μm , which goes far beyond traditional media printing and printed optoelectronic devices such as solar cells made of thin semiconductor layers of about 1 μm . For this reason, we are investigating screen printing as a possible manufacturing technique for the mass production of thermoelectric modules and energy storage devices. This thesis explores the limit of screen printing technology for thick films/patterns

and proposes new functional inks to deposit four main classes of materials: insulators, polymer electrolytes, organic and inorganic semiconductors and metals.

Several questions arise and constitute more specific aims of the thesis:

- (i) *Can we formulate an ink to create a thick layer of a thermoelectric semiconductor, an ionic thermoelectric polymer, a polymer electrolyte, a mixed ion-electron conductor? Is it feasible to maintain the electronic or ionic conductivity or the Seebeck coefficient as high as possible in these thick layers?*
- (ii) *How thick and with what resolution can the functional materials - insulator, organic semiconductor, metal or a polymer electrolyte - be screen printed without reducing the lateral resolution with increasing thickness? How can the viscosity be increased without losing the electrical and thermoelectric properties of the layers? Can we print cavities of an insulator and fill them with low viscosity semiconductor ink or electrolyte ink by multiple print runs and ensure adequate lateral resolution?*
- (iii) *How can it be ensured that the upper layers do not adversely affect the lower layers when multilayer structures are printed?*

Figure 2. Schematic illustration of kind of conductor and principle design of the devices.

2 Fundamentals

In this chapter the basics of the two main topics of the thesis, thermoelectric generators and electrochemical energy storage, will be covered. The principle mechanism as well as the fundamental differences in the composition of the devices will be discussed.

2.1 Thermoelectrics

Three thermoelectric effects named after their discoverers Thomas J. Seebeck, Charles A. Peltier and William Thomson (Lord Kelvin) are linked by the Kelvin relations. The Seebeck effect has gained much interest in the past, since it is the underlying principle of converting thermal energy directly into electricity. Thermoelectric generators (TEGs) based on the Seebeck effect have no moving parts and are maintenance free devices, important issues for long-term usage in harsh environments. Therefore TEGs were and still are being used for instance for NASA space missions ^[13]. Nowadays, TEGs are recovering some energy in the combustion system of cars. The reverse effect was found by Peltier. Thermoelectric coolers (TECs, Peltier devices) are used in portable refrigerators or in lab devices for cooling purposes. Thomson developed the Kelvin relations and predicted the Thomson effect that describes the reversible heat transport in a conductor in which an electrical current flows.

2.1.1 Basic Thermoelectric Equations

If the ends of a metal rod or wire are held at two different temperatures, the electrons on the hot side have more kinetic energy than on the cold side. Thermodiffusion between the hot and the cold side develops until the electric field prevents further separation. Hence, the electric potential at the cold side is more negative than at the hot side, see Figure 3.

A thermoelectric voltage is developed between the positively charged hot end and the negatively charged cold end, due to the potential difference. The open circuit potential difference is a material parameter called the Seebeck coefficient:

Figure 3. Thermodiffusion of charge carriers due to the temperature difference between both ends of the conductor ^[14].

$$S = \frac{dV}{dT} \quad (1)$$

with the Seebeck coefficient S in $\text{V}\cdot\text{K}^{-1}$, potential difference dV in V and temperature difference dT in K. The performance of thermoelectric (TE) materials is determined by a dimensionless figure of merit ZT defined as

$$ZT = \frac{S^2 \sigma}{\lambda} T \quad (2)$$

with electrical conductivity σ in $\text{S}\cdot\text{m}^{-1}$

$$\sigma = \frac{l}{R \cdot A} \quad (3)$$

where l is the length of the conductor in m and R is the ohmic resistance in Ω and A is the cross-sectional area of the conductor in m^2 . The thermal conductivity λ in $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ is defined as

$$\lambda = -\dot{q} \cdot \left(\frac{\Delta T}{\Delta x} \right)^{-1} \quad (4)$$

where $\dot{q}$ is the heat flow per cross-sectional area in $\text{W}\cdot\text{m}^{-2}$ created by the temperature difference ΔT in K over the thickness Δx in m.

The numerator $S^2 \sigma$ in equation (2) is called power factor. ZT is an important parameter for comparing TE materials. The Seebeck coefficient S to the power two is dominating the equation, but the quotient of electrical and thermal conductivity σ and λ is also crucial, since these parameters are often linked, e.g. in metals.

The theoretical maximum efficiency of a heat engine is determined by the Carnot efficiency η_{carnot}

$$\eta_{\text{carnot}} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} \quad (5)$$

with the temperature at the hot end T_h and the temperature at the cold end T_c .

The efficiency of a TE device is directly related to ZT . For power generation, the efficiency η is given by

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}} \quad (6)$$

It is important to use materials with a high ZT value for practical applications^[15]. Thermoelectrics will provide only a fraction of the carnot efficiency, e.g. if $ZT=1$, $\Delta T = 100$ K, $T_c = 300$ K, efficiency η can reach 5%.

2.1.2 Thermoelectric Generators and Coolers

If two dissimilar thermoelectric materials are electrically connected, the device is called a thermocouple (TC). See Figure 4 (a). The thermoelectric materials are also known as legs, which are characterised by the majority charge carriers accumulating upon thermal diffusion. If the majority charge carriers are electrons that accumulate at the cold end, the Seebeck coefficient of the material is negative. In contrast, if holes accumulate at the cold end, the Seebeck coefficient is positive. This is valid for metals but also for semimetals and semiconductors. Semiconductors are distinguished in p- and n-type materials, according to the majority charge carriers. This indication is also common with thermoelectric legs.

When a temperature gradient is applied between the junction and the open ends of the TC, a thermoelectric voltage is created. Many of these TCs electrically connected in series and thermally in parallel are called thermoelectric generator (TEG), see Figure 4 (b).

The top and the bottom of a TEG are made of a thermally conducting, electrically insulating material, e.g. ceramics, in order to have a low thermal resis-

Figure 4. (a) A thermocouple consists of two dissimilar materials connected by a conductor. (b) The electrical series connection of several to many thermocouples is called thermoelectric generator (TEG).

Figure 5. Ragone plot of selected energy storage devices ^[17].

tance to the TEG, but to prevent short-circuits. The designs of either a TEG or thermoelectric cooler (TEC) are the same, the only difference is that one device is connected to and powering a load; the other one is connected to a current supply, which creates a heat current occurring in the TEC, establishing a hot and a cold side.

In the conventional TEG/TEC production the thermoelectric material bismuth telluride (Bi_2Te_3) is commonly used for low temperature applications (<200 °C). A combination of an electron conducting n-type material and a hole conducting p-type material represents the thermoelectric legs of a TC ^[16]. A good electrical conductor, e.g. copper, connects the legs. The height of the legs is in the order of millimetres to ensure a large temperature gradient. The series connection is realised by a three-dimensional meander structure with alternating electrical connections on the top and bottom of the device.

2.2 Electrochemical Energy Storage

The debate on energy storage is omnipresent. Whether in the field of renewable energies or electromobility, the performance and safety of electrochemical systems are always under discussion. In the laboratory environment, performance is of primary interest. This can be equally evaluated for batteries and supercapacitors by determination of the specific volumetric or gravimetric capacity/capacitance and how quickly this energy is provided to the load or how fast the energy storage can be recharged.

(a) Stack Design

(b) Coplanar Design

Figure 6. Schematic of printed batteries and/or supercapacitors (a) in a stacked layout and (b) in a coplanar design.

There are fundamental differences between batteries, conventional capacitors and supercapacitors with regard to the relevant performance data, as shown in Table 1 and the Ragone plot in Figure 5. The latter shows the in the storage device available specific energy on the y-axis and the specific power on the x-axis. The diagonal lines represent the time frame in which the device may be charged and discharged.

Both energy storage devices examined in this thesis share the same principle layouts. Either the stack design or the coplanar layout may be used for creating printed supercapacitors or batteries, as illustrated by Figure 6.

2.2.1 Supercapacitors

The term supercapacitor comprises electric double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors, see Figure 7. If the capacitance is mainly determined by the development of a Helmholtz double layer, the term EDLC is used. When faradaic processes are involved, the term pseudocapacitor is used.

Table 1. Comparison of characteristics of energy storage devices ^[22,23].

Factors	Batteries	Conventional Capacitors	Electrochemical Capacitors
specific power (W/kg)	50-200	$\gg 10\,000$	500-10 000
specific energy (Wh/kg)	20-100	< 0.1	1-10
charge time	0.3-3 h	10^{-6} - 10^{-3} s	1-30 s
discharge time	1-5 h	10^{-6} - 10^{-3} s	1-30 s
cycle life (cycle)	10^3 - 10^4	$> 5 \times 10^5$	10^5 - 10^6
charge/discharge efficiency (%)	70-85	100	90-95

A hybrid supercapacitor is the combination of both ^[18,19]. The composite artificial word supercapattery ^[20] may also be used.

Supercapacitor is a class of devices that are able to store a huge amount of charge. The technology was developed in the 1980s as a bridge between capacitors and batteries. The energy storage mainly takes place at the interface of the microporous electrode and the electrolyte. Highly porous activated carbon is one of the most important electrode materials in supercapacitors. However, an increase in energy density is possible by using other electrode materials in addition to activated carbon ^[21].

Supercapacitors provide higher specific power but lower specific energy than batteries ^[22,23], see Table 1. Thus, supercapacitors are intended to be used in applications in which transient power peaks are required without the need for a high capacity.

An important feature of supercapacitors is the short charge and discharge time. Supercapacitors can be charged and discharged within seconds. Possible applications are therefore energy recovery systems, e.g. for dynamic braking of transport systems ^[23].

The operating voltage of a supercapacitor depends on the electrolyte used. The voltage must be selected so that the electrolyte does not degrade during operation. The basic structure of a supercapacitor comprises two opposing electrodes, which are electrically separated by a separator soaked with electrolyte. The separator must prevent electrical contact between the two electrodes, but at the same time enable a high ionic conductivity. The best results are achieved with

Figure 7. Classification of supercapacitors in subcategories, according to ^[21,23].

Figure 8. Principle of an electrochemical double layer capacitor. (a) Helmholtz introduced an explanation based on rigid layers. (b) Stern, Gouy and Chapman refined that model by introducing a diffusion layer additionally to the rigid Helmholtz layer.

separators of small thickness ^[23]. Both electrodes are made of the same material in the symmetrical version. In the asymmetrical version, two different electrode materials are used, a capacitive electrode and a pseudo-capacitive electrode.

The design of supercapacitors is similar to the design of other capacitors e.g. electrolytic capacitors. The basic principle of a parallel plate capacitor model holds true also for supercapacitors, but on a much smaller scale of the dielectric layer. Furthermore, the charge storing area is very large due to the highly porous electrode materials. Supercapacitors are therefore able to store up to several hundreds of Farads.

Parallel Plate Capacitor Model

A plate capacitor is determined by the area of the opposing electrically conductive plates i.e. electrodes, the distance and the material between those electrodes, as expressed by the following equation

$$C = \frac{Q}{V} = \epsilon_0 \cdot \epsilon_r \cdot \frac{A}{d} \quad (7)$$

with total charge Q in C transferred at potential V in V, the capacitance C in F, the dimensionless relative permittivity ϵ_r , and the dielectric constant ϵ_0 of the dielectric between the electrodes in $\text{F} \cdot \text{m}^{-1}$, opposing plate area A in m^2 , and distance between the electrodes d in m.

Electrical Double Layer Capacitor

The electrodes of an Electrical Double Layer Capacitor (EDLC) are made of highly porous materials, providing a huge surface area. Between the electrodes

there is an electrolyte with more or less free moving ions. By charging the electrodes, the ions with the opposite polarity accumulate at the electrode-electrolyte interface forming an electrical double layer (EDL). German scientist Hermann Ludwig Ferdinand von Helmholtz discovered the formation of the EDL. The Inner Helmholtz Plane (IHP) is formed by the solvent in which the electrolyte is dissolved, thus, this plane is very thin, see Figure 8.

This is followed by the outer Helmholtz plane (OHP) with the solvated ions, i.e. ions surrounded by a tiny shell of solvent. The thickness of IHP and OHP is approximately between 0.1 and 10 nm. The short distance between the electrode surface and the solvated ions induces, analogous to the dielectric in the parallel plate capacitor model, a charge on the carbon electrode. Both factors, the very large surface area due to highly porous electrodes and the tiny distance between the electrode and the ions add up to a large capacitance, hence the name supercapacitor.

Pseudocapacitor

In contrast to non-faradaic processes occurring in EDLC, pseudocapacitors rely on fast and reversible redox reactions between the electrode and the electrolyte. Pseudocapacitance arises at the electrode surfaces, involving the passage of charge across the double layer, similar to batteries ^[24]. Electrodes may be made of transition metal oxides e.g. RuO_2 or conducting polymers like PEDOT:PSS. Electrodes made of RuO_2 adsorb and desorb hydrogen, theoretically providing a gravimetric capacitance of $1358 \text{ F} \cdot \text{g}^{-1}$ ^[25]. In conducting polymers the energy is stored by doping and dedoping. In Table 2 the specific advantages and disadvantages of conductive polymers and transition metal oxides are shown ^[26].

The redox reactions correspond to an electron transfer process between an oxidised and a reduced species. A thermodynamic interdependency between the extent of charge acceptance Δq and the change in potential ΔV allows capacitance to be determined by derivative $d(\Delta q)/d(\Delta V)$ or dq/dV ^[27,28].

Hybrid supercapacitors are made of capacitive (EDLC) and pseudocapacitive electrodes. This combination offers a high capacitance due to the pseudocapacitive electrode and a high energy density due to the capacitive electrode. The advantages and disadvantages of pseudocapacitive electrodes compared to

Table 2. Advantages and disadvantages of pseudocapacitor materials ^[26]

Conductive Polymers		Transition Metal Oxides / Sulfides	
e.g. polyaniline and polythiophene		e.g. MnO_2 , RuO_2 , TiS_2	
<u>Advantage</u>	<u>Disadvantage</u>	<u>Advantage</u>	<u>Disadvantage</u>
solution processing*	short lifetime	high specific capacitance	short lifetime
cyclability	self-discharge		low conductivity
			poor ion permeability
			costs
* room temperature			

Table 3. Comparison of pseudocapacitive with capacitive electrodes ^[29].

Advantage	Disadvantage
higher energy density in general relatively flat discharge profile	less potential power-density cycle-life depends on charge/discharge rates, and depth of discharge less cycle-life different performance dependency on temperature than capacitive electrode

capacitive electrodes are shown in Table 3.

2.2.2 Batteries

In general, electrochemical energy sources convert chemical energy directly into electrical energy without any intermediate step. In contrast to other energy conversion processes, this results in high energy efficiency. At least two reagents are involved in the conversion, which react chemically during the process and can provide electrical current to an external circuit at a voltage defined by the reactants i.e. the electrochemical system.

The term battery relates to a series or parallel connection of single electrochemical cells, the so-called galvanic element. By series connection, the rather small cell voltage of a single electrochemical cell could be increased, by parallel connection, the capacity is increased accordingly.

Primary cells supply energy only once and are not rechargeable, at least not to a significant extent. With Zn/MnO₂ cells, the electrochemical system often used with printed batteries, a few discharge/charge cycles are possible, but the aqueous electrolyte is consumed during discharge. Another deficiency in this system is the dendrite formation in zinc, which occurs when the cells are charged. Dendrites may penetrate the separator, short-circuiting the electrodes and thus may render the cell unusable.

Secondary cells can be recharged, i.e. the chemical reaction is reversible, so that the external circuitry determines, if the cell is charged or discharged. The reversibility of the chemical reaction is imperfect, therefore the cyclability of the cells is limited. It is claimed by the manufacturers that modern cells may be cycled over 1000 times. Depending on the discharge/charge time frame this implies an unrealistic lifetime, which definitely exceeds the stability of the battery packaging itself ^[30]. Therefore, it often makes more sense to indicate the service life of the cell instead of the cycle stability.

In Figure 9, an electrochemical cell is shown. The two electrodes, anode and cathode, are separated by an ion-permeable separator. In the external circuit, electrons flow while the charge exchange inside the cell takes place via ions in the electrolyte. The resistance of the electrolyte determines the amount of current which could be drawn from the cell. Thus, for high current applications, the re-

sistance should be low, which may in turn accelerate the self-discharge process. The term self-discharge describes the phenomenon that an electrochemical cell loses charge without a connected consumer. This loss of charge is due to internal chemical reactions caused by impurities of reactants and electrolyte. The course of self-discharge depends on various factors such as cell chemistry, ambient temperature and the state of charge. The self-discharge determines also the shelf-life of batteries ^[31]. Figure 9 shows the discharge process, after which the negative electrode is referred to as the anode and the positive electrode as the cathode in commercially available batteries.

Figure 9. Principal illustration of an electrochemical cell in discharging situation.

3 Functional Screen and Stencil Printing

Screen and stencil printing has been used for technical applications for many decades. The printed circuit board was already conceived in the 1940s and has been produced on an industrial scale ever since ^[4]. The conductive structures of the printed circuit board are produced by means of etching resists. Solder resist and label print are also applied by screen printing. The miniaturisation of the electronic components was also made possible by stencil printed solder paste for the preparation of paste depots used in the reflow process. Stencil printing shows its strengths in the application of high ink film thicknesses, using pastes containing large solder particles.

3.1 Screen Printing vs. Stencil Printing

Screen printing is a frequently used process in printed electronics, as the applied layer thicknesses can be deliberately adjusted over a wide range. In addition, the meshes and especially the threads are increasingly becoming finer, so that line widths below 50 μm are already reproducible and the resolution limit is shifted further down. For instance, the authors in ^[32] report of fine line printed silver ink structures on silicon heterojunction solar cells as fine as 34 μm in width.

The printing forms in screen and stencil printing differ only in one point, which, however, has a great effect on the printed image and the printing result. In screen printing, the mesh is used as a stencil carrier, which also holds internal image elements (island) in place, which in stencil printing can only be achieved

Figure 10. Schematic side views of screen printing and stencil printing.

Figure 11. Printing forms – (a) screen printing with the mesh as the stencil carrier holding internal image elements (island) in place. (b) Stencil for stencil printing of solder paste.

using bars that interfere with the printed image, see Figure 11 (a) and (b). In addition, the printing process differs in that screen printing involves filling the open mesh with ink using a floodbar before printing and transferring the ink to the substrate using a squeegee in a further step. Flooding is not applicable with stencil printing, as no threads in the open image elements can hold the ink. Thus, in both stroke directions a squeegee is used.

In screen printing, it can be advantageous to set a distance between substrate and stencil, the so-called snap-off distance, since during the printing process the mesh is stretched under print pressure, ink splitting takes place in the contact zone between the printing form and substrate, and certain factors can cause the substrate to be lifted off the vacuum table. In stencil printing the stencil must be in good contact with the substrate in order to prevent the ink to move under the stencil, and thus, achieve a sharp edged print result, see Figure 10.

What both methods have in common is that the attainable ink layer thickness can be controlled by the stencil thickness. However, above a certain structure width, the choice of mesh thickness or thread diameter is more important in screen printing than the thickness of the EOM (emulsion over mesh). Coarse meshes with thick threads and large mesh widths achieve a high ink film thickness. The coarser the mesh, the more the resolution is reduced as not all fine details can be held on the mesh. In stencil printing only the thickness of the stencil is important. This determines the theoretical ink volume that can be deposited on the substrate. Similar to screen printing, the structure width also impacts the ink layer thickness. If a particular structure size is exceeded, the squeegee may sink into the aperture (stencil printing) or analogously presses the screen deeper down, so that less ink will be transferred. This behaviour is more pronounced with polymer squeegees than with metal blades ^[33].

The printing process itself also offers parameters that influence the result, such as the shape, angle and hardness of the squeegee as well as the printing speed. The number of settings offers great flexibility in the printing process and

can be adapted to many requirements depending on the rheological properties of the liquid to be processed, the substrate or other specifications ^[34].

Screen printing can be implemented in the process in various machine configurations. Flatbed machines in different automation levels, rotary roll-to-roll machines or hybrid solutions using flat screens on roll materials are used on an industrial scale.

3.2 Mesh Type

The mesh as the stencil carrier is important and provides some crucial properties that impact the print results. Meshes can be made of nylon, polyester (PET) or stainless steel. The latter requires careful handling and is more expensive than the polymer alternatives, but it offers some advantages like smaller thread diameter or higher percentage of open area. In Table 4 the distinctive advantages of the two commonly used mesh materials are shown.

Table 4. Comparison of the advantages of PET and stainless steel mesh

Polyester Mesh	Stainless Steel Mesh
flexibility	high strength
robustness	low elongation
mechanical stability	printing of hot-melt possible
	high percentage of open area
	high resistance against climate changes (temperature and humidity)

Trampoline screen

With a trampoline mounted screen the advantages of PET/nylon, stainless steel or cut/etched stencils are combined by making use of a composite print form. The stainless steel mesh is mounted on polyester mesh, which is then partly removed. This combination provides the absorbance of induced mechanical stress by the surrounding and enduring polyester mesh and the precision and fine threads of the stainless steel mesh. The resulting print form is less prone to being damaged. Costs are reduced, since less of the expensive stainless steel mesh is used. It is also possible to attach a metal or polymer stencil instead of the stainless steel mesh.

3.3 Thick Film Printing

For achieving a thick ink layer with one printing stroke, the mesh is one of the most important factors. A coarse mesh will transfer a high ink volume onto the substrate. But the resolution of the printed image may suffer from a coarse mesh, since a wide mesh width is not able to hold tiny image elements as precisely as a smaller mesh opening. Alternatively, several successively printed layers on top of each other may also establish the required ink layer thickness. This is only

possible if the previously printed layer may be dried or cured within the printing machine, i.e. without removing the substrate from the print table. Otherwise, it is most likely to provoke register misalignment. With UV curing ink it is possible to build up several layers of the same print image with a precise register within a reasonable period of time.

Thick film printing in screen printing mostly depends on the thickness of the mesh. The thread diameter and the weaving of the mesh govern the thickness of the mesh. A smaller contribution to the transferable wet ink film thickness is made by the stencil thickness. The theoretical ink volume V_{th} , in $\text{cm}^3 \cdot \text{m}^{-2}$ as depicted by Figure 12 and equation (8), depends on the percentage of open area α_0 , and the mesh thickness D in μm .

$$V_{th} = \frac{\alpha_0 \cdot D}{100} \quad (8)$$

Since the total ink volume will not be released from the mesh, the true value of the wet ink thickness is 10 to 30 % less than calculated ^[34]. The influence of the stencil must additionally be considered.

Figure 12. Nomenclature of screen meshes, schematic illustration of percentage of open area, mesh thickness and theoretical ink volume according to ^[35].

3.4 Stencil

For screen and stencil printing, a stencil containing the image information is required. The type of stencil differs fundamentally. In screen printing, a photosensitive polymer is used, which is exposed using a lithographic mask. The photosensitive polymer film is applied as wet emulsion or as direct or indirect film to a screen mesh, the so-called stencil carrier. It is also possible to use a pre-coated mesh, which is tensioned on the screen frame already containing the photosensitive layer ^[36]. With stencil printing, the imaging elements can also be structured using mask exposure, but afterwards an etching process is required. However, laser cut stencils can nowadays usually be produced more economically. The stencil production used for screen printing in the course of this work is shown in Figure 13.

Figure 13. Schematic illustration of used processes for applying photosensitive material on the screen mesh. (a) Machine coating and (b) manual coating of emulsion, (c) manual application of capillary film. Created after ^[37].

3.4.1 Emulsion and Capillary Film

Different stencil materials for screen printing are available: liquid emulsion and direct as well as indirect film. Emulsions are made of UV curing materials that are applied on the mesh by a coating trough (scoop coater). This could be done manually or automatically with an automatic screen coating machine. The indirect and direct films are based on PET films that were previously coated with photosensitive material in a continuous coating process. Both emulsion and films are usually exposed to UV light using a lithographic film. Direct films are applied on the screen mesh before exposure and development; indirect film is applied after the two process steps. The capillary film is applied after the mesh was wetted with water so that it will be partially sucked into the mesh. Alternatively, it is possible to bond the film to the mesh with liquid emulsion, which is necessary for film thicknesses $> 150 \mu\text{m}$.

Specially developed emulsions are available for the many applications in screen printing, e.g. for thick-film printing or high-resolution stencils. The emulsions differ mainly in the chemical reactants, the mechanical and chemical resistance and their viscosities. Capillary films are also available in thicknesses up to several hundred microns.

One advantage of using a capillary film is the precisely defined thickness of the emulsion applied to the PET film. The continuously coated film also results in a small surface roughness (R_z) of the photosensitive material on the film. Thus it is possible to obtain a reproducible stencil on the mesh. The drawbacks of the film are higher costs and weaker adhesion to the mesh. The result is a shorter lifetime of a stencil made by film.

3.4.2 Stencil Manufacturing

Stencils can be made by three different processes, of which two are subtractive: chemical etching and laser cutting. The third process electroforming is an additive process, which results in a different surface topology.

Laser Cut Stencils

Laser cut stencils are usually made from thin metal sheets and represent the most frequently used stencils for the production of microelectronic components. The advantages of this technology are the low machine costs, as well as the speed and flexibility of the process. Since each opening in the metal sheet has to be cut individually, the time and costs increase with the number of structures to be cut. Applications with a large number of openings are therefore inefficient. During the laser process, minimal areas are strongly heated, so that the material melts. This can lead to distortions on the surface and unclean cut edges that cause the side walls of the opening to have a rough edge that affects the release of the paste. Rolled stainless steel sheets are often used for printing stencils, the crystal structure and alloy composition of which influence, for example, the release of paste ^[38].

Despite the good laser spot resolutions and sufficient energy density of the laser beam, the laser cut structures in the side walls of the openings sometimes exhibit a certain roughness that can be caused by impurities in the base material.

In addition to stainless steel sheets, nickel panels or polymer sheets are also used as stencil material. Nickel shows a better release of the paste from the openings than stainless steel stencils. Polymer stencils made of polyimide provide very precise stencils due to the lower roughness of the inner edges of the cut openings. For an optimal result, the relevant parameters such as power, frequency and cutting speed must be adjusted ^[39].

In Do-It-Yourself and Maker scene ^[40] very often PET sheets are used to apply solder paste on self-made printed circuit boards. High quality stencils are made of aluminium sheets in various thicknesses. With the stencil thickness the applied ink layer thickness is governed. Most stencils are laser cut, but etching is also possible.

Chemically Etched Stencils

Similar to the production process of printing screens, chemically etched stencils made of brass or stainless steel base material are provided with a photosensitive layer. This layer is exposed and developed via a lithographic film. The chemical etching process follows during which the areas not covered by the cured photosensitive material are removed. Due to the polycrystalline structure of the base material, different etching rates are effective at crystal boundaries

Figure 14. Influence of stencil processing on the aperture shape, according to ^[33].

Table 5. Comparison of stencil technologies, according to ^[41].

Stencil Technology	Accuracy	Resilience	Production Time	Paste Yield	Cost/ Performance
etched	-	+	++	+	+
laser cut	+++	+++	+++	+++	+++
electroformed	+++	+++	+	+++	+++

during the isotropic etching process, which is noticeable in a slightly porous structure of the inner walls of the etched openings. This porosity influences the release of the printing paste. Due to the process-related tapered shape of the openings, see Figure 14, the resolution of the etched stencil is limited ^[38]. Etching may lead to errors in the stencil production like under or over etching. A comparison of stencil production methods is shown in Table 5.

3.5 Drying Mechanism of Printing Inks

The drying mechanism of printing pastes is an important feature with regard to the manufacturing process. Depending on drying behaviour, fast rotary roll-to-roll presses or slower sheet-fed presses can be used. With sheet-fed presses, often the printed sheets are removed from the machine and subjected to a thermal treatment. It must be ensured that the accuracy of registration of the subsequent printing steps is guaranteed. In roll-to-roll production, the printing layer that has been previously applied must be dried or cured before the next guide roller is reached. Metal particle filled printing inks often require thermal treatment to achieve proper percolation (see 4.1.2) of the functional particles. On the other hand, UV curing systems are often used for insulating printing inks, allowing the printed layer to cure quickly.

3.5.1 Physically and Chemically Drying Inks

The physical drying of the printing layer describes the evaporation of solvents so that a dry ink layer remains on the substrate. Many printing inks used in technical screen printing work according to this principle. In chemical drying, on the other hand, the solvent is not removed, but chemically modified. This drying behaviour is not to be found in functional screen printing but in offset printing, which in turn does not play an important role in printed electronics. In terms of electrically conductive inks the evaporation process allows for controlling the formation of percolation networks. A fast evaporation of the solvent will lead to higher mechanical stress but also an improved electrical contact between the conductive particles. The mechanical stress can lead to a lower adhesion to the substrate ^[42]. A compromise between electrical conductivity and mechanical properties must be found.

3.5.2 Inks Requiring Irradiation or Elevated Temperature

UV curing inks are widely-used in the graphic arts industry due to their advantages^[43]. Solvent based inks require thermal treatment after printing. Duration and temperature of the thermal treatment depends on the evaporation time of the used solvents and the thickness of the ink film. The processing time of UV-curing inks is drastically shorter. This enables faster production, for instance, multi-layer designs can be printed one after the other in a shorter time. Other benefits of UV inks are the reduction of volatile organic compounds (VOC), the lower energy consumption, no clogging in the stencil apertures and the stacking of the printed substrates without blocking, to mention just a few^[44].

The curing of UV inks is initiated by the chemical reactions between the monomers/oligomers and the photoinitiators. Long-chain polymers are formed from the short-chain oligomers during polymerisation. Two principles of polymerisation are mainly used in printing inks: the cationic and the radical polymerisation.

Free Radical Polymerisation

UV inks based on the free radical polymerisation contain acrylate oligomers, which are responsible for the adhesion, mechanical resistance and flexibility of the ink film. Acrylic monomers are also added to adjust the viscosity. Various additives are used for adjusting the thixotropy (see 6.2.3), surface wetting, stability against sedimentation, etc. The photoinitiators are the most prominent part of a UV ink, since they provide the free radicals for the polymerisation reaction induced by irradiation with light of a specific wavelength. The photoinitiators split by absorbing the energy of the UV irradiation into free, unsaturated radicals. These radicals are now able to crosslink the oligomers forming long-chain polymers that are stable against solvents and heat. This process repeats until termination, i.e. reaction of radical with initiator radical or another monomer/polymer radical or chain transfer takes place, which is initiation of a new chain, see Figures 15 and 16. An inert atmosphere is advisable for radical polymerisation, since oxygen inhibits the reaction on the ink's interface to air. The polymerisation only takes place while UV irradiation is applied.

Figure 15. Process of UV light induced curing according to^[45].

Figure 16. The steps of free radical polymerisation initiated by UV light. Propagation and Chain Transfer lead to long polymer chains. Termination ends the curing process.

Cationic Inks

Usually epoxy resins and photoinitiators based on arylsulfonium salts are used in cationic UV inks. By irradiation with UV light, the photoinitiators are broken down into an acid catalyst. Saturated cycloaliphatic epoxies have a good resistance to environmental influences and are frequently used due to this property ^[46].

Once started, the polymerisation in cationic UV inks does not stop, even in the absence of irradiation. Cationic photoinitiators decompose to propagate the polymerisation. Cationic inks are superior to radical systems, when adhesion on difficult substrate is problematic ^[47]. Cationic inks are not affected by air oxygen; there is no oxygen inhibition. However, cationic systems are susceptible to humidity; a diminished adhesion could be the result and due to several other reasons (economic, fast process, depth of cure), the majority of UV inks in screen printing are radical systems.

Elevated Temperature Treatment

Plastisol inks are usually used in graphic applications for screen printing textile designs, mainly t-shirt imprints. Plastisol inks are possible candidates for being used as thermal and electrical insulators, since the resins of plastisol inks are polymers and therefore show insulating properties. In plastisol inks, polyvinyl chloride (PVC) particles of 0.1 to 0.2 μm in size are dispersed in plasticisers. Plasticisers lower glass transition temperature T_g and the softening temperature, as well as the mechanical stability of the polymer. Plasticisers also reduce the intermolecular forces between the polymer chains ^[48]. Curing of plastisol is possible by heating. The polymer dissolves irreversibly in the plasticiser, when the glass transition temperature of the polymer is reached, forming a soft PVC film. The plasticiser penetrates the PVC-particles, which then swell. When all the plasticiser is absorbed, the plastisol is gelled ^[49]. Fusion, the state when the PVC micro crystallites have fully melted, takes place between 120 $^\circ\text{C}$ and 190 $^\circ\text{C}$ ^[50]. Additives like epoxies are used for improving the resistance to heat. Plastisol inks are inexpensive and show high adhesion and durability on several substrates ^[51].

3.6 Ink / Substrate Interactions

In printing technology, the interaction of printing fluid and substrate is of great importance, as the printing quality depends on the suitable material com-

bination. There are a large number of ink formulations and substrates with different properties, so that it is essential to assess the wettability of the substrate by the ink. Wetting describes the extent to which the printing ink is capable of adhering to a substrate. Complete wetting is referred to as spreading, see Figure 17. The quality of the wetting can be determined, e.g. by contact angle measurement.

Surface tension and free surface energy are equivalent physical terms; the first is usually used for liquids and the second for solids [52]. Surface tension in liquids derives from less neighbouring molecules at the surface of e.g. a droplet. This imbalance causes liquids to contract into an energetically favourable spherical form. The increase in surface requires work. This principle also applies to solids and surface free energy, which usually have to be measured indirectly, e.g. by its wettability and thus with the help of the contact angle.

Young's equation establishes a relationship between the contact angle θ and the surface tension of the liquid and the solid phase, γ_{LV} and γ_{SV} .

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cdot \cos(\theta) \quad \text{or} \quad \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos(\theta) \quad (9)$$

with the contact angle θ , the interfacial tensions between the solid and the vapour γ_{SV} , the liquid and the vapour γ_{LV} , and the liquid on the solid γ_{SL} , see Figure 18.

A frequently used procedure to determine the contact angle of a known liquid on a unknown substrate is the sessile drop method. A drop of known volume is applied to the surface to be examined and evaluated using drop shape analysis (DSA). The contact angle is determined using a camera system that generates a grayscale image for contour evaluation on the computer. Thus, the contact angle can be determined by applying a tangent to the triple point of the solid/liquid/vapour phase transition. DSA is also used in the pendant drop method, which allows the evaluation of the surface tension or interfacial tension of the liquid.

Even if the contact angle is measured and the surface tension of the test liquid is known, there are two other unknowns, namely the surface energy of the solid γ_{SV} and the interfacial tension between the solid and the liquid γ_{SL} . When studying the surface energy of the solid, the interfacial tension between solid

Figure 17. Exemplary wetting behaviour of liquids on substrates. Good wetting is crucial for high print quality.

Figure 18. A drop of a well-known liquid applied on a substrate reveals the contact angle θ , which allows for calculation surface free energy of the substrate.

and liquid must be determined. Various models can be used for this purpose, of which the Owens-Wendt-Rabel-Kaelble (OWRK) model is very common, especially in the investigation of printing inks. It is based on the work of Frederick Fowkes^[53]. The OWRK model determines the disperse and polar components of the surface tension of liquids and the surface free energy of solids, see equation (10). The use of only two test liquids already provides a good agreement between the empirically determined results for wettability and adhesion and the values calculated according to OWRK. Nevertheless, it is advisable to use more than two liquids.

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \cdot \sqrt{\gamma_{SV}^D \cdot \gamma_{LV}^D} + \sqrt{\gamma_{SV}^P \cdot \gamma_{LV}^P} \quad (10)$$

The superscript letters indicate the type of component with D = dispersive and P = polar. The free surface energy of the solid is determined by using at least two liquids whose disperse and polar components of the surface tension must be known. One of the liquids must have a polar component > 0 . One advantage of the OWRK process is that the influence of polar and disperse interactions on wettability and adhesion becomes apparent, so that it is frequently used for coating, printing and bonding^[54].

4 Materials

Printed electronics is an exceptionally interdisciplinary working field which, in addition to process engineering, also covers the fields of materials science and electronics. It is crucial to establish a liquid compatible with the application process. In addition to the intrinsic material properties exploited in the particular application, the used compounds must also ensure processability. Any additives required for wetting, stabilisation or rheological optimisation of the printing ink usually show a tendency to deteriorate the desired function. Conventional printing inks are already complex systems with often numerous components. Consequently, functional inks, e.g. silver inks, carbon-black, battery electrode inks etc. are at least similarly complex formulations. In order to minimise the influence on the function, an approach can be to reduce the additives to a minimum. However, there is a fine line between the functionality of the printing paste and its processability in the printing process, so that compromises have to be made in one direction or the other.

4.1 Functional Printing Inks

The intentional creation of structures with graphic printing inks serves to convey information, either in the form of letters, symbols or as image elements. In the field of functional printing, the information-transmitting properties of printing inks are generally omitted. Functional materials must usually have a precisely specified property, e.g. electrical conductivity.

Traditional compositions of conventional printing inks are often inappropriate, since the optimisation for the printing process may contain components that impair their functionality. The formulation of functional pastes is therefore a critical part of printed electronics, which has a decisive influence on the performance of the components produced by printing technology.

4.1.1 Dielectric Inks

In printed electronics, non-conductive polymers (NCPs) are used as insulators and substrates. NCPs are saturated polymers, i.e. all electrons take part in σ bonds. The band gap of the NCPs is wide enough that there is no electrical conductivity. Many different types of polymers are used in technical screen printing inks, which are suitable as thermal and electrical insulators because their material properties are comparable. The most important difference is the printability and processability of the material. The latter is strongly depending on the curing mechanism. Rapid curing by means of UV radiation is the ideal solution for printing inks that are used as an insulating layer. On the one hand, fast print sequences can be implemented. On the other hand, it is also possible that several layers are printed on top of each other with intermediate curing.

4.1.2 Particle Filled Functional Inks

The conductivity in metal-filled polymer pastes depends directly on the filling grade of the conductive pigments. The percolation threshold marks the amount of particles in the polymer matrix that is necessary to establish electrical pathways, as shown in Figure 19.

If the percolation threshold is not met, the conductivity of the paste will be very low, or even non-existent. At low fill levels, the particles are not in contact, but if the distance is small and the oxide is thin enough, tunnelling between the particles is possible, i.e. there is low electrical conductivity despite no contact between the particles. At the percolation threshold or critical concentration, the resistance is drastically reduced by the significantly increased contact area between the particles ^[55].

Conductive inks are normally highly filled with conductive (metal) particles such as silver, activated carbon, nickel, manganese dioxide etc. The filling grade depends on the requirements of the application such as electrical conductivity. Highly viscous inks are stable and prevent sedimentation while being stored ^[55]. The amount of varnish (binder and solvent) decreases with an increasing filling grade, leading to a poorer coating of the particles. Agglomeration could lead to clogging of the printing screen ^[56]. Additionally, the ink's cohesion and adhesion will degenerate dramatically while the viscosity will simultaneously rise. Heavily filled inks behave more like slurries than printing inks.

Due to the underlying principle, the electrical conductivity achieved by percolation pathways is always lower than that of the solid. By means of sintering, i.e. the actual fusion of the functional particles into a solid, the electrical conductivity can be brought into the order of magnitude of the bulk material. However, this requires high temperatures and other ink formulations that may not be compatible with flexible, polymeric substrates. These sinter pastes are used, for instance, in photovoltaics to print the bus bars of the current collectors.

Figure 19. Schematic of percolation in functional printing inks. The percolation threshold marks the establishment of electrical pathways.

Figure 20. Percolation paths of (a) flakes and (b) spheres ^[60], (c) spheres of different diameters ^[63], (d) spheres and (e) elongated particles with aspect ratio > 1 . (f) A mixture of elongated particles (nanorods) and small spheres displays the lowest resistivity ^[65].

A gentler approach is offered by photonic sintering, which applies the high energy required to fuse the conductive particles only locally ^[57,58]. With this process, flexible substrates can also be used, which would be destroyed under the high thermal loads of conventional sintering processes. Melting point depression is a well-known phenomenon in nanotechnology ^[59], which is also used in photonic sintering. With nanoparticles, the fusion of the particles already begins with a lower energy input than with coarser particles, so that the printed structures and the substrate have to withstand less thermal stress. This also enables using materials such as copper, which does not function as conventional printing paste, since an electrically insulating oxide layer is immediately formed on the particles. By attaining local temperatures up to 1000 °C ^[58], photonic sintering melts the metallic copper into a bulk, so that the conductive path is not affected by copper oxide on the metal surface.

The shape of the particles is also of interest. Very often metallic flakes are preferred ^[60]. These flakes are able to form denser layers during thermal processing than spherical particles, see Figure 20 (a) and (b). Spheres are forming electrical pathways through rather small contact points between individual particles with higher contact resistances than flakes which are characterised by having a larger contact area ^[61]. Additionally, during the evaporation of the solvent, the ink film shrinks, resulting in denser flake sheets. This compression effect may be less pronounced with spheres, since the hardness of the particles prevent compression and thus no increase in contact area is noticeable. A mixture of flakes and spherical particles with small diameters or spheres with different diameters are supposed to form a large number of electrical pathways with only a few voids ^[62,63], see Figure 20 (c). High conductivity at low filling factor can be achieved by using conductive fillers with a high aspect ratio (length : width), as shown in Figure 20 (f) ^[64]. The use of spherical particles requires a higher fill factor than that of elongated particles with a higher length/width ratio. The percolation probability of 50% is the same in both Figure 20 (d) and (e). This is achieved with

spherical particles with a filling factor of approx. 55 % in (d), whereas for the elongated particles (c) with an aspect ratio of 8 a filling factor of only 31 % is required ^[65].

4.2 Conducting Polymers

Traditionally, polymers (poly = many, mer = unit) are valued for their chemical, mechanical and electrical resistance. But since the discovery of intrinsic electrically conductive polymers in the 1970ies and the possibility of doping (in chemical terms: oxidation and reduction), conducting polymers found interest in many new applications, such as optoelectronics, printed electronics ^[66], supercapacitors, micro actuators ^[67], bioelectronics ^[68], etc. This class of material combines unique features, such as solution processability, lightweight, flexibility, and special optical and electrical properties. Because of the ground nature of this discovery, A. Heeger, A. Mc Diarmid and H. Shirakawa were awarded the Nobel Prize in Chemistry in 2000. Polymer electronics is also named organic electronics, since carbon is the backbone of conducting polymers.

In the early valence bond theory, bonds in organic molecules were explained from the atomic electronic structure and the notion of hybrid orbitals. The electronic configuration of the carbon atom in its ground state is: $1s^2 2s^2 p_x^1 p_y^1$, i.e. two electrons are able to form two covalent bonds. In order to explain that in methane carbon has four bonds, one introduced the notion of “promotion”. That is, assume that electrons can be excited and occupy higher energy levels. The energy cost of this excitation will be balanced by the stabilisation energy due to the creation of several bonds using those excited electrons. A modification of the ground state is necessary to have four half-filled orbitals.

If one electron from the 2s-orbital is elevated into the p_z -orbital, the carbon atom is in an excited state with the configuration $1s^2 2s^1 p_x^1 p_y^1 p_z^1$. In this excited state, four covalent bonds are possible. Since there are three half-filled p-orbitals and one s-orbital, the bonds would not be identical. However, one can consider instead that four new hybridised orbitals named sp^3 will be established as linear superpositions between the 2s-orbital and the three p-orbitals. With this notion of hybrid orbitals, the four identical bonds in methane are rationalised, see Figure 21. The energies of the sp^3 -orbitals are lower than that of the p-orbitals, but

Figure 21. Electron configuration of carbon atoms.

Figure 22. Schematic illustration of alternating double and single bonds. For each C-atom the p_z -orbital is perpendicular to three sp^2 -orbitals that are in one plane (120°). The p_z -orbitals of adjacent atoms are overlapping in π -orbitals forming a π -bond besides the σ -bond.

higher than that of the 2s-orbital, since three p-orbitals and one s-orbital contribute energetically to the hybrid-orbital.

4.2.1 Conjugated Polymers

In conjugated polymers (CP), the carbon atoms are sp^2 -hybridised. The sp^2 -orbitals of each carbon atom are sitting in one plane forming σ -bonds with three sp^2 -orbitals of adjacent atoms. The two-lobe shaped p_z -orbital is perpendicular to the plane formed by the sp^2 -orbitals of each atom. The electrons in p_z -orbitals of adjacent carbon atoms are able to form π -bonds. Hence, there is a double bond (σ - and π -bond) between two adjacent carbon atoms, see Figure 22. Conjugated polymers are characterised by an alternation between single and double bonds along the chains of carbon atoms. Sometimes other atoms such as oxygen, sulphur or nitrogen atoms are involved in the conjugated paths.

Electrical conduction is possible through the π -bonds. Electronic charge carriers are delocalised and move along the polymer chain without introducing any bond cleavage in the skeleton of the chains. Indeed the latter is maintained by the σ -bonds. Conjugated systems are also called Intrinsic Conductive Polymers (ICP). The repeat units of some ICPs are shown in Figure 23.

A polymer is a chain of atoms. To understand the electronic structure of conjugated polymers, one should first remember the simplest model: an infinite chain of hydrogen atoms. Each hydrogen atom has one 1s-electron. The chain is

Figure 23. Intrinsically conductive polymers – 1) polyacetylene, 2) polyaniline (PANI), 3) thiophene, 4) polypyrrole, 5) poly (3,4-ethylenedioxythiophene) (PEDOT) ^[69].

Metallic Equidistant System

Semiconducting Alternating System

Figure 24. Schematic illustration of the Peierls-distortion. The alternating bond lengths achieve an energetically lower state, thus the system is more stable ^[70].

characterised by a 1s electronic band that is half-filled. This then is the electronic structure of a metal. In conjugated polymers, we first assume that the distance between the carbon atoms is similar, due to σ -bonds. The focus is on the electronic structure resulting from the remaining one $2p_z$ -electron per carbon atoms. A half-filled π -band is formed. Again, this corresponds to the electronic structure of a metal. In reality however, conjugated polymers are not intrinsically metallic, but rather insulators or semiconductors. Indeed, a polymer chain with equal bond length between each carbon atoms in the conjugated path is not energetically stable. As a result, there is a Peierls-distortion that decreases the symmetry of the system and stabilises it, see Figure 24. This distortion is the creation of a bond length alternation between the carbon atoms and results in a band gap between the valence band and the conduction band.

The width of the gap between the valence and the conduction band determines whether a material is a conductor, a semiconductor, a semimetal or an insulator, see Figure 25. In the case of organic conductors the highest occupied molecular orbital (HOMO) is the upper edge of the valence band. Accordingly, the lowest unoccupied molecular orbital (LUMO) is the lower edge of the conduction band. Organic semiconductors also have a band gap between the HOMO and LUMO, similar to inorganic semiconductors. With increasing conjugation length, the band gap decreases.

Figure 25. Band filling of metals, insulators, semiconductors, and semimetals. Position of the Fermi energy (dashed line) and width of the band gap are used to classify the materials.

Doping

In its pristine form, the electrical conductivity of CP is close to those of traditional insulators. By oxidation (p-doping) the charge carrier density increases and the polymer becomes electrically conductive. Analogous to inorganic semiconductors, the doped charges result in gap states ^[71]. The doped charges are not only a charge in excess on the polymer chain, but they are also associated with a localised distortion on the polymer chain, i.e. the structure in the proximity of the doped charge is distorted. The charges with a local relaxation are forming quasiparticles. These charged quasiparticles could be called solitons, polarons and bipolarons, depending on their characteristics ^[72]. Solitons only exist in degenerate ground state CP, e.g. polyacetylene, in which the interchange of single- and double bonds does not affect the energy of the polymer. In non-degenerate ground state polymers there are polarons and bipolarons. Polarons or bipolarons (higher concentration) are created, depending on the concentration of added charge carriers. The longer the conjugation length and the higher the doping level of the CP, the more localised states exist in the band gap, creating a band.

Electrochemical Doping

Either a two-electrode set-up with a working and a counter electrode or a three-electrode set-up with an additional reference electrode is used for electrochemical doping. Three electrodes allow for precise monitoring and controlling of electrochemical parameters. With electrochemical doping, the doping level can be adjusted accurately. The process is reversible, i.e. doping and dedoping is possible without removing chemical products ^[73,74]. As with chemical doping, a counter ion is also required with electrochemical doping, in order to stabilise the charge along the polymer backbone ^[73].

Photo Doping

Photo doping is the effect of significantly increasing the electrical conductivity of a polymer by irradiation. Doping occurs when the radiation energy is greater than the band gap of the polymer. It is a volatile effect, since the recombination of free electrons and holes takes place rapidly and the creation of free electrons stops when irradiation stops ^[75], but “the application of an appropriate potential during irradiation could separate electrons from holes, leading to photoconductivity.” ^[73] With photo doping there are no counter ions.

Charge-injection Doping

Charge carriers can “be injected into the band gap of conjugated polymers by applying an appropriate potential on the metal/insulator/polymer multilayer structure”^[75], analogous to the function of a FET. Like photo doping, charge-injection doping is a volatile process that generates no counter ions.

Non-redox Doping

In contrast to the aforementioned ways of doping, the number of electrons associated to the polymer backbone do not change when applying the non-redox doping route. “The most studied doping process of this type is the protonic doping of polyaniline emeraldine base (PANI EB) with aqueous protonic acids, such as HCl.”^[73] With non-redox doping “the conductivity is increased by a nine to ten order of magnitude.”^[75]

Secondary Doping

Primary doping of conducting polymers changes the material properties, amongst others the electrical conductivity. By removing the dopant also the changes in material properties will vanish. If a second dopant is used supplementary to the first dopant, the material properties are further modified. Although the impact of the secondary dopant is smaller than of the primary dopant, the modification of the secondary dopant may be persistent even when it is removed^[76]. In the case of polyaniline, secondary doping leads to crystallinity even in the dispersion as well as in the solid polymer film. On the other hand, PEDOT:PSS films stay amorphous using secondary dopants and the effect of the secondary dopant only applies to the conformation of the polymer film when it already has been formed^[77].

4.3 Thermoelectric Materials

The figure of merit $ZT = S^2 \cdot \sigma \cdot T / \lambda$ implies that reasonable thermoelectric materials show a high electrical conductivity σ and a low thermal conductivity λ . Material researchers in thermoelectricity aim for “electron crystals” and “phonon glasses”, i.e. the material should have the electrical conductivity of crystalline metals and the low thermal conductivity of glass.

The electrical conductivity σ depends on the particular electronic structure of the material. Metals yield high electrical conductivity, since the conduction

band is partly filled, allowing the electrons to move freely along the crystal structure of the metal. The electrons are referred to as free electron gas, if no interactions with the lattice ions are considered. In this simple model, the thermal conductivity of metals is virtually only dependent on the free electrons, so that the thermal conductivity is also high.

The rate of heat flow in heat conducting material is described by Fourier's law of thermal transport for 1D transport along the length Δx

$$\dot{Q} = \frac{dQ}{dt} = -\lambda \cdot A \cdot \frac{T_2 - T_1}{\Delta x} \quad (11)$$

with the rate of heat flow $\dot{Q}$ in W, heat Q in J, and time t in s. The thermal conductivity λ is in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, the area subject to the heat flow A in m^2 , the cold and hot ends T_2 and T_1 in K, and the distance of the examined heat flow path Δx in m.

The total thermal conductivity $\lambda = \lambda_L + \lambda_E$ is constituted by the lattice and the electronic thermal conductivity, λ_L and λ_E respectively. For pure metals it is valid to assume $\lambda_E \gg \lambda_L$. The Wiedemann-Franz law defines the dependency of the electrical conductivity σ and thermal conductivity λ in metals

$$\frac{\lambda}{\sigma} = L \cdot T \quad (12)$$

with the Lorenz number $L = 2.44 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ [78] and the absolute temperature T in K.

In contrast, the thermal conductivity of insulators only depends on lattice contribution (phonons) [79].

The Seebeck coefficient S of metals and degenerated semiconductors, i.e. highly doped semiconductors, is defined by

$$S = \frac{8\pi^2 k_B^2}{3eh^2} \cdot m^* \cdot T \cdot \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \quad (13)$$

with the Boltzmann constant $k_B = 1.380645 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$, effective mass of charge carriers m^* in kg, temperature T in K, elementary charge e in C, the Planck constant h in J·s or eV·s, and carrier concentration n in m^{-3} [80, 81].

The electrical conductivity σ derives from

$$\sigma = n \cdot |e| \cdot \mu \quad (14)$$

Figure 26. Illustration after ^[82] showing the dependency of the Seebeck coefficient on electrical conductivity and carrier concentration respectively.

with the charge carrier concentration n , carrier mobility μ in $\text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, and absolute elementary charge $|e| = 1.602177 \times 10^{-19} \text{ C}$.

If the charge carrier concentration n is increased, the Seebeck coefficient S decreases according to equation (13) and the electrical conductivity increases, according to equation (14), see Figure 26.

The Fermi energy of metals is located within a band, which is half-filled due to an odd number of electrons per unit cell. The Fermi energy of insulators is located in the middle of the band gap between the valence and conduction band. This band gap is larger than the thermal or photonic energy that could excite an electron from the valence band into conduction band without destroying the insulator.

The band gap of intrinsic, undoped semiconductors is smaller than that of insulators, such that electrons can, for example, be elevated from the valence to the conduction band by thermal excitation. The Fermi energy is also located in the middle of the band gap, analogue to insulators. The position of the Fermi energy of doped semiconductors is either shifted towards the conduction band (n-type) or the valence band (p-type). In semimetals there is no band gap. A small overlap of the valence and conduction band (e.g. $E_g = 0.02 \text{ eV}$ for Bi) may even exist ^[83].

The Seebeck coefficients of metals are less than $50 \mu\text{V} \cdot \text{K}^{-1}$, whereas in semiconductors several hundreds of $\mu\text{V} \cdot \text{K}^{-1}$ can be achieved ^[84]. Semimetals, e.g. antimony (Sb) or tellurium (Te), have lower thermal conductivities than metals, and although their electrical conductivities are smaller than those of metals, these materials are appropriate for thermoelectric applications ^[85], see Table 6.

Table 6. Material properties of metals, semiconductors, and insulators ^[86].

Properties	Metal	Semiconductor	Insulator
$S (\mu\text{V} \cdot \text{K}^{-1})$	~ 5	~ 200	~ 1000
$\sigma (\Omega^{-1} \cdot \text{cm}^{-1})$	$\sim 10^6$	$\sim 10^3$	$\sim 10^{-12}$
$Z (\text{K}^{-1})$	$\sim 3 \times 10^{-6}$	$\sim 2 \times 10^{-3}$	$\sim 5 \times 10^{-17}$

Comparing the purity of the material in correlation with the electrical conductivity provides a clear distinction between a semiconductor and a metal. The conductivity of metals decreases with impurities, since impurities appear as a scattering site for the electrons. The conductivity of semiconductors increases when the impurities are dopants.

Another difference between metals and semimetals, as well as semiconductors, lies in the fact that the conductivity of metals/semimetals decreases with increasing temperature, because electron-phonon scattering is promoted at high temperature. In contrast, the conductivity of semiconductors increases because the Fermi distribution extends more in the conduction band and valence band with increasing temperature, so that the charge carrier density increases with the temperature. The conductivity is proportional to the product of the charge carrier mobility and charge carrier density; see equation (14).

For some decades ZT was around unity, see Figure 27. Intensive research in materials science led to new TE materials exceeding unity by several fold. Established thermoelectric materials, which are used in commercial applications, could be divided into three groups, depending on the temperature range of operation^[88]. The low temperature materials in the range of up to 450 K are mainly based on Bi in combination with Sb, Te and Se. A frequently used material combination in this temperature range is the previously mentioned Bi_2Te_3 , both the n-type and the p-type. Lead and alloys made thereof are best used in the intermediate temperature range from 450 to 850 K. Silicon germanium alloys are chosen for the highest temperature range up to 1300 K.

There are many other materials that also have aroused interest by research groups, namely thermoelectric oxides, skutterudites and the like. Besides the many TE materials, new approaches are found in improving the dimensionless figure of merit ZT of thermoelectric materials mostly through the reduction of

Figure 27. (a) The carrier concentration of 10^{19} cm^{-3} (= semiconductor) provides the maximum ZT and is a trade-off between electrical and thermal conductivity^[87]. (b) The evolution of ZT for some thermoelectric materials between 1950 and 2010^[15].

Figure 28. (a) Earth abundance of established TE materials with world reserves (circle) and annual world production (squares). (b) The price per kg correlates with the abundance ^[92].

lattice thermal conductivity via introduction of nanostructure or by modification in the atomic range ^[89].

Organic conductors e.g. PEDOT, PANI and TTF-TCNQ ^[90,91] and the like have attracted interest since they typically possess a very low thermal conductivity (0.3-0.8 Wm⁻¹·K⁻¹) and a moderate electrical conductivity (up to 3000 S·cm⁻¹) ^[85]. The abundance of atomic elements used in organic conductors is another advantage over inorganic materials ^[92], see Figure 28. They are also non-toxic. Mixtures of organic conductors with inorganic thermoelectrics are also proposed.

4.3.1 Recent Advances in TE Materials

Superionic conductors are promising materials achieving $ZT > 2$ in high temperature application, but stress tests are pending, so that the thermal stability of the electric conduction are still to be proven ^[93].

TEGs on flexible fabrics are a subject that recently gained importance, confirmed by a considerable number of publications in this field that have appeared in recent years. Sunmi Shin et al. ^[94] reported p-type BiSbTe and n-type BiTeSe legs stencil printed on flexible glass fabrics with a Seebeck coefficient S of 209 $\mu\text{V}\cdot\text{K}^{-1}$ and -165 $\mu\text{V}\cdot\text{K}^{-1}$ in p-type and n-type materials respectively. The printed p-type is very close to the value of the bulk material, which is 220 $\mu\text{V}\cdot\text{K}^{-1}$.

Organic thermoelectrics only have a low solids content in the printing paste. Compared to inorganic materials, less thick layers can be produced by printing. Gordiz et al. ^[95] offer a solution to this problem by increasing the filling factor to 91% using an hexagonal design instead of aiming for thick functional layers. The use of Hilbert connection patterns enables the production from roll to roll and the creation of customised designs. The authors' concept is to adapt the design parameters of organic TEGs to take advantage of the unique properties of organic materials and achieve high-performance devices.

Ferhat et al. ^[96] published an organic n-type formulation for inkjet printing. The researchers have developed a composite material made of PEDOT and

vanadium pentoxide gel, generating a power density of $0.266 \mu\text{W}\cdot\text{cm}^{-2}$ at 20 K temperature difference.

4.3.2 Bi and Sb Containing Printing Inks

Bismuth is the most promising thermoelectric material in conventionally produced thermoelectric generators in the temperature range below 200 °C. An alloy of Bi and Te is widely-used both in thermoelectric generators and in Peltier devices. Sb also shows a considerable high Seebeck coefficient. From the process perspective all the aforementioned materials are lacking in compatibility with already existing ink formulations (binder-solvent matrices) established for low temperature metal-filled polymer inks. Like other metal particles that are not usable for low temperature printing inks due to their tendency to oxidise, Bi_2Te_3 as well as Bi and Sb are similar to Al, Cu and the like. Printing inks consisting of these particles may be available, but not in the low temperature regime^[97,98] or only in combination with more complex treatment processes after printing, such as photonic sintering^[99].

Other printing methods are utilised^[100,101], so that the ink does not have to meet the rheological requirements of screen printing. Additionally, the abundance of these materials is low but the toxicity is rather high – two attributes that are obstructive for a mass application of printed thermoelectric generators based on Bi and Te. Bi and Sb are considered to be amongst a list of critical raw materials^[102]. Nevertheless, some research institutes are working on methods for the application of Bi, Te or Sb containing inks on flexible substrates in the higher^[97], as well as lower temperature range^[103,104].

4.3.3 Nickel Printing Inks

In the manufacturing of printed circuit boards (PCB) and electronics, nickel is one of the important metals to pattern conductive tracks. Usually, the base material of a PCB is copper, which is prone to oxidation. A gold layer is used to protect the traces and contacts from corrosion. A diffusion barrier consisting of a Ni layer between the Cu and Au layer provides long-term stability of the traces and contacts. Although nickel is widely-used in electronics, it is a toxic allergen suspected of causing cancer and this may be why many manufacturers of Ni printing inks withdrew their products in the past. Ni ink is still available, but only from a few manufacturers.

Metallic Ni oxidises slower than e.g. Cu or Al, hence there is no need for inert atmospheres during the mixing of the ink. Processing of the particles into a printing paste is less complex, as no sophisticated laboratory equipment is required. Due to their poor malleability, Ni particles cannot be produced as flakes that promise high conductivity, see Figure 20. However, Ni inks are used in shielding applications, as well as in anisotropic or isotropic conductive adhesives^[62].

4.3.4 PEDOT:PSS

The co-polymer PEDOT:PSS consisting of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) is one of the most important conductive polymers in the field of printed electronics. PEDOT:PSS is important because it is stable in an aqueous solution, which opens up a wide range of processing methods. For example, PEDOT:PSS can be used as printing ink in different processes. Commercially available products are tailored to the respective rheological requirements, so that PEDOT:PSS is a component of many investigations in inkjet^[105], gravure^[106], flexographic printing^[107] and screen printing^[108]. It is used in thermoelectric applications, and as a transparent layer in touchpad and electrochromic applications^[109]. PEDOT itself is not soluble in water. However, the addition of PSS as the counterion enables a stable water emulsion^[26].

The deprotonated PSS is the negative counterion and the p-type dopant, stabilizing the charge on the PEDOT^[110]. Basically PEDOT:PSS achieves a conductivity of $1000 \text{ S}\cdot\text{cm}^{-1}$ ^[111], but there are also publications, such as Worfolk et al., which report $4600 \text{ S}\cdot\text{cm}^{-1}$ ^[112]. By choosing the type of counterion for PEDOT stabilisation, the conductivity can be adjusted. For instance, the complex PEDOT:TOS has proven high electrical conductivity and a high Seebeck coefficient^[113]. The chemical structures of PEDOT:PSS and PEDOT:TOS are shown in Figure 29.

4.3.5 Ionic Thermoelectric Materials

Another promising class of materials is developing under the term ionic thermoelectrics, whose function has already been demonstrated in TE modules^[114], ionic thermoelectric sensors^[115], and ionic thermoelectric supercapacitors^[116]. Solid-state polyelectrolytes show great potential for thermoelectric generators in flexible applications e.g. in wearables. In^[117] the authors report a Seebeck coefficient of up to $5.5 \text{ mV}\cdot\text{K}^{-1}$ with the proton conductors Nafion and sulfonated poly (ether ether ketone) (S-PEEK). The anion conductor poly(diallyldimethylammonium chloride) (PDDAC) provides a Seebeck coefficient of $19 \text{ mV}\cdot\text{K}^{-1}$.

Figure 29. Chemical structure of (a) PEDOT:PSS and (b) PEDOT:TOS, two important conducting polymers often used in thermoelectric applications.

At an applied temperature gradient, thermodiffusion also takes place with ions, which is described by the Soret effect ^[118]. The charge carrier density of a typical electrolyte is about the same as that of a typical semiconductor and lies between 10^{19} and 10^{22} cm^{-3} ^[119]. However, ions suffer from lower mobility than electrons, since they are larger and heavier. Thus, conductivity is lower and typically it lies between 10^7 and $10^{-1} \text{ S}\cdot\text{cm}^{-1}$, while the ionic Seebeck coefficient is approximately $500 \mu\text{V}\cdot\text{K}^{-1}$ ^[120]. However, very high Seebeck coefficients of up to $10 \text{ mV}\cdot\text{K}^{-1}$ have already been reported by several research groups ^[121–123]. Since the ions do not pass into the external circuit and instead form a Helmholtz double layer on the electrode surface (see 2.2.1), the charge current approaches zero over time, provided there is a constant temperature difference ^[124]. As such, the device incorporates energy conversion and storage in one component.

Devices with ionic thermoelectric materials must therefore provide large electrode surfaces in order to act as an ionic thermoelectric supercapacitor (ITESC) ^[120, 123] and store as much thermal energy as possible in the form of electric charges.

Due to the time dependency of the process, an ITESC is ideally suited for intermittent heat sources. A further advantage of the ITESC principle is the higher amount of energy that can be stored in this integrated component when compared to the series connection of two discrete components, namely a thermoelectric generator (TEG) and a supercapacitor ^[120].

The huge Seebeck coefficient of polymer electrolytes, see Figure 30, has generated interest in new research directions, such as thermo-electronic circuits that use heat as an input signal or ultra-sensitive temperature sensors that can

Figure 30. Seebeck coefficients of ionic, organic and inorganic thermoelectric materials. Ionic conductors show high Seebeck coefficients.

compete with pyroelectric devices ^[125]. Polymer electrolytes are of interest because they resemble a solid rather than a liquid (see 4.4.3). This is an advantage especially with regard to the ion-electronic circuits mentioned above. It is also conceivable that the enormous Seebeck coefficient can be used reasonably in combination with other polymer electrolyte-based components, for example in electrochromic displays ^[126], ion pumps ^[127], ionic bipolar diodes ^[127], and electrochromic bipolar membrane diodes ^[128].

4.4 Energy Storage

Printed supercapacitors and batteries can be made using the same design. It is even possible to obtain a battery or a supercapacitor just by changing the electrode inks. There are not only overlaps in the structure of the two components, but also some of the functional principles are the same. Batteries, for instance, assume faradaic processes, which can also occur in supercapacitors depending on the choice of material. A supercapacitor can therefore also be seen as a combination of electrochemical double layer capacitor and battery, as described by the artificial word supercapattery ^[20]. This closeness of the components in theory and in their actual form enables the examination of both components without much effort.

4.4.1 Supercapacitor Electrodes

There are a variety of electrode materials that are suitable for use in supercapacitors ^[129–131]. Frequently used materials are shown in Table 7. Many supercapacitors are based on the principle that a high surface area of the electrodes is used to store charge. This high surface area is mainly achieved by activated carbon electrodes, which are extremely porous. The production of activated carbon is based on a wide variety of starting materials. Usually organic materials are carbonised at high temperatures with the help of other chemical substances, resulting in a porous material with a definable number and size of pores.

4.4.2 Battery Electrodes

Lithium-based battery systems provide high energy densities and lead to powerful cells, so that this material is frequently used. However, the applicability in screen printing is limited by the high reactivity of Li and is only possible if the material is applied in an inert atmosphere. Nevertheless, there are research groups

Table 7. Materials for supercapacitor electrodes

EDLC	Pseudocapacitor
activated carbon	organic conductors, e.g. PEDOT:PSS
graphene	transition metal oxides, e.g. MnO ₂ , RuO ₂
carbon nano tubes	

that also use screen printing to produce Li-based batteries ^[132]. Polymers have also been used as electrode material. However, the performance of these is low ^[133,134].

Due to their easy processing, primary cells of the Zn/MnO₂ type are often screen printed. The materials offer the advantage of not requiring a special atmosphere and are thus quite easy to process. Rechargeable secondary cells have also been published with these electrode materials. However, Zn tends to form dendrites during charging, which eventually destroy the battery. There are approaches to suppress the growth of dendrites, so that this chemical system is also available for use in rechargeable printed batteries ^[135].

Due to the environmental sustainability and simplicity of the well-known zinc-manganese system ^[136], it was chosen for the investigation of the influencing variables and optimisation of the parameters. Although cells of this type are already commercially available, hardly any or only limited information can be found in scientific publications about which combination of components results in the highest possible performance. The overall reaction of a ZnCl₂-Cell ^[137] is as follows:

By the stoichiometry of the involved reaction partners it can be calculated that the reaction is significantly controlled by the amount of MnO₂. The calculated mass ratio between MnO₂ and Zn is 2.66:1. According to literature ^[138], however, it can be assumed in real application that this ratio must still be shifted by a factor of two in the direction of MnO₂. Consequently, there is a strong imbalance in the electrode masses to be applied. The higher density of Zn of about 7 g·cm⁻³ compared to about 5 g·cm⁻³ of MnO₂ makes it even more difficult to apply ink layers complying with the required mass ratio.

4.4.3 Electrolytes

The operation of electrochemical cells is based on the combination of electronic and ionic conductivity within a system. The electronic conductivity is reserved for the external circuit and the internal processes use the ionic conductivity of the electrolyte. In an electrolyte, the conducting ions are more or less dissociated in a solvent. The degree of dissociation is a measure for the weakness or strength of the electrolyte. Strong electrolytes are acids or bases that dissociate completely or to a high extent. Electrolytes are chemical compounds that can be in a solid, liquid or dissolved state. The main classes of electrolytes used in printed electronics application are shown in Figure 31. It is of importance for the particular printing method to use electrolytes providing the appropriate viscosity, thus more viscous electrolytes may be necessary, for instance, in screen printing.

Electrolytes are often divided into aqueous and non-aqueous systems. With aqueous solvents, the potential window is limited to 1.23 V, where the electro-

Figure 31. Types of electrolytes according to ^[139].

lysis of water starts. Non-aqueous solvents allow for a higher operation voltage window. The maximum voltage is important since it determines the amount of energy that can be stored in a supercapacitor, according to the equation (15)

$$E = \frac{1}{2} \cdot C \cdot V_{max}^2 \quad (15)$$

with energy E in Joule (or W·s), capacitance C in F, and maximum operation voltage V_{max} in V.

The simplest electrolyte system, the electrolyte solution, consists of salts dissolved in solvents. The solvated ions have high ionic conductivity and at the same time low viscosity. The potential window depends on the used solvent.

The Stokes-Einstein equation (16) relates the mobility of the ionic charge carrier and its assumed radius to the viscosity of the electrolyte solution. In the simple model, the hydrodynamic radius is spherical ^[140]

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta \cdot r} \quad (16)$$

with diffusion coefficient D in $\text{m}^2\cdot\text{s}$, Boltzmann constant k_B in $\text{J}\cdot\text{K}^{-1}$, absolute temperature T in K, dynamic viscosity η in $\text{Pa}\cdot\text{s}$, the mathematical constant π , and the effective radius of the spherical species r in m.

In a general form of the Einstein relation the diffusion coefficient depends on the mobility of particles and temperature

$$D = \mu \cdot k_B \cdot T \quad (17)$$

It is noteworthy that the charge carrier mobility μ occurs in equation (17) as well in equation (14), $\sigma = \mu \cdot |e| \cdot c$, the latter being the definition of the electrical conductivity.

Ionic liquids (IL) are salts with large ions, mostly organic cations and organic or inorganic anions, which by common agreement are molten salts with a melting point less than 100 °C. IL showing a melting temperature lower than 25 °C may further be categorised as room temperature ionic liquids. The low melting point is derived from weak ionic bonds, but at the same time the ionic conductivity is rather high ^[141]. Key properties of ILs are low-vapour-pressure, non-flammability ^[142], and a large potential window ^[143], so that ionic-liquid-based electrolytes are interesting candidates in batteries, supercapacitors, fuel cells and ionic thermoelectric supercapacitors. For processing reasons, ILs can be incorporated in hosting polymers including block copolymer ^[144] or polyelectrolyte ^[145]. The liquid is then named ion gel, a polymer network swollen by an ionic liquid, which consist of only a small amount of polymer and thus retains an ionic conductivity comparable to the one achieved by the constituting IL ^[139].

In polyelectrolytes an electrolyte group, e.g. salts, acids and bases, is incorporated in the repeat unit of the host polymer. Since the polymer is rather long, this electrolyte group is quasi immobile in solid dry polyelectrolytes. With the addition of a polar solvent, the electrolyte group is able to dissociate. As such, the polymer chain is charged and surrounded by solvated counterions, which are free to move. Positively charged polyelectrolytes are called polycations, while polyanions are negatively charged ^[146].

Polymer electrolytes are solvent-free dissolutions of salts in a viscous polymer host providing ionic conductivity and are thus utilised in a number of printed electronics applications, such as batteries, supercapacitors, solar and fuel cells, electrochemical sensors and ionic thermoelectric supercapacitors ^[147]. Polymer electrolytes may be categorised into solid, gel and composite polymer electrolytes (SPE, GPE, and CPE), see Figure 32.

The advantages of polymer electrolytes are the avoidance of internal short-circuits, leakage of electrolytes and the generation of flammable reaction products at the electrode, which is in contact with the liquid electrolytes. Com-

Figure 32. Categorisation of polymer electrolytes, according to ^[147].

pared to solid and liquid electrolytes, GPEs are considered superior in terms of voltage, specific capacity, service life, charging and discharging speed, among other things ^[148].

Conduction Mechanism

Ion transport in electrolytes can generally be distinguished according to two principles. With diffusion, the ions move due to a concentration gradient, while with electromigration, an applied electric field leads to charge transport by ions ^[139]. The ionic conduction mechanism depends on the type of electrolyte.

In aqueous systems, the proton conduction takes place by the Grotthuss mechanism, as shown in Figure 33, which leads to high ionic conductivity through the rearrangement of hydrogen bonds ^[149,150].

Polyelectrolytes are characterised by solvated counterions. The ions including the solvent shells are moving as a whole through the electrolyte and are experiencing a frictional force proportional to the viscosity of the solvent and the size of the solvated ion.

In polymer electrolytes, the ion transport is facilitated by sites that are created and destroyed on a continuous basis as a result of segmental motion of the polymer chains ^[152], due to flexibility of the polymer chains in disordered regions

Figure 33. Illustration of the Grotthuss mechanism after ^[151]. a) The grey proton forms a hydrogen bond to a water molecule as a part of a hydrogen-bonded chain. b) Along the chain, hydrogen atoms are hopping to the neighbouring sites. c) Proton released at the end of the chain. d) By rotation, the water molecules end up in the original orientation. e) The whole process starts again.

with sufficient open space allowing for fast ionic transport ^[153]. Thus, crystalline regions in the polymer will reduce the ionic conductivity.

4.4.4 Separator

Although the choice of the appropriate separator depends on the chemical system of the electrochemical cell, there are some aspects that are important for all separators. First of all, the chemical resistance of the separator material to the electrolyte must be guaranteed. Depending on the desired cell properties, the selection of the separator can be used to adjust the internal resistance. Highly porous separators achieve a low internal resistance so that high currents are possible. However, the high porosity leads to limitations of the mechanical strength. Less porous separators are mechanically stronger and offer long cell life without

Table 8. Overview of processes in nonwoven production ^[154].

Web Formation	Web Bonding	Finishing
dry-laid	bonding agents	wetting agents
wet-laid	thermobonding	corona/plasma
spunbond	needling (mechanical)	gas-phase fluorination
meltblown	hydro-entanglement	acrylic acid grafting
		wet-phase sulfonation

load or low self-discharge, but less charge/discharge current. Optimisation and compromise approaches must therefore be found.

Separators must prevent short-circuits between the electrodes. They also ensure that particles detached from the electrode do not cause defects. The wettability of the separator should be high so that it can be well penetrated by the electrolyte. This wetting should also be guaranteed over a long period of time ^[154].

Printed electrochemical cells utilise two different separator types: nonwovens and solid electrolyte systems that can be printed. Nonwovens are technical fabrics that are not woven but rather form a three-dimensional fibre network due to different manufacturing processes. The fibres are made of polymers according to the required properties the nonwoven separator must meet. The origin of the polymer could be natural or synthetic, e.g. cellulose and polyester respectively. Table 8 shows different processes in the production of nonwovens. During production, the processes of the first and second columns run simultaneously, the processes attributed to finishing are executed afterwards.

From a processing point of view, the use of printable separators is advisable since the current collectors and the electrodes are printed. If the separator can also be printed, the machine configuration is less complex. If a nonwoven is used, it must be placed after the electrodes have been printed and dried, which increases the complexity of production. In addition, the use of a gel polymer electrolyte (GPE) meets the requirements of printed and portable applications through a high degree of flexibility and elasticity of the separator film.

The investigation of a screen-printable GPE based on cornstarch in paper VI takes these circumstances into account. The starch hydrogel was chemically modified using citric acid and, in addition to the rheological properties, the ionic conductivity and thus the function as gel electrolyte are also determined by means of citric acid.

State of the Art in Starch Gel Polymer Electrolyte

Hydrogels are often used as printable solid electrolytes that offer an adjustable viscosity but also high porosity for water-like liquids. This material class can also be produced on a natural or synthetic basis. Polysaccharides (cellulose, starch, etc.) are often used as starting materials for natural, hydrogel-based printable separators.

Table 9. Starch-based polymer electrolytes reported in literature.

Ref.	Binder	Plasticiser	Salt	Conductivity [$\text{S}\cdot\text{cm}^{-1}$]
[155]	starch	glycerol	LiCl, NaCl, KCl	
[156]	starch	-	NH_4NO_3	2.83×10^{-5}
[157]	cornstarch	AMIMCl	LiTFSI	4.18×10^{-4}
[158]	cornstarch	glycerol	LiOAc	1.04×10^{-3}
[159]	cornstarch	-	LiPF_6 , BmImPF ₆	1.99×10^{-4} (80 °C)
[160]	cornstarch	glycerol	NH_4Br	1.80×10^{-3}
[161]	potatoe starch, PVA	glycerol	LiBr, nano	1×10^{-3}
[162]	food grade cornstarch	-	fumed silica	3.39×10^{-4}
[163]	potato starch	glycerol	LiTFSI	1.61
[164]	wheatstarch, gelatin	-	LiI	8.5×10^{-1} , 7.2×10^{-1} (gelatin)
[165]	lignocellulose	-	NaCl	1.27×10^{-3}
	and potato starch		LiPF_6	

As indicated by Table 9, hydrogels are attractive for many research groups all over the globe. From the simple, natural ones, such as gelatin, that we all know from cooking [166], chemists have found different routes to synthesise hydrogels and modify them to their wishes [167–169]. Hydrogels are enriching our daily life, for instance in the form of soft contact lenses, invented and firstly applied by Chemist Otto Wichterle in 1962 [170], in tissue engineering [171] and pharmaceuticals, e.g. in drug delivery [172]. Besides artificial, petrochemical-derived hydrogels, natural biopolymers have important characteristics such as high abundancy and bio-compatibility, low costs and high availability. One of the main disadvantages of natural products is the fluctuation in quality and thus the reduced reproducibility of the chemical properties. Polysaccharides as starch [173], cellulose [174], xanthan gum [175] and the like are able to form natural, native hydrogels. Such materials are used, for instance, as rheological modifiers [176] in many commodities like shower gels, cosmetics and in food processing [177], as well as in technical applications e.g. paper making [178] and printing inks [175].

The properties of native starting materials may be modified by combining of bio- and synthetic polymers, e.g. by grafting [179]. Otherwise, synthetic polymers can be made biocompatible by adding a biopolymer, what makes the material more eco-friendly [180, 181].

Hydrogels can absorb large amounts of water by swelling up (10-1000 times the initial weight) [182]. This property is used e.g. in diapers [183]. The majority of hydrogels increase their volume by water retention, thus leading to a more amorphous inner gel structure.

Hydrogels are polymer networks that can be physically or chemically cross-linked. Starch as a representative of polysaccharides is able to form hydrogels

just by heating. Even this simple physically modified hydrogel is already useful, e.g. as wallpaper paste ^[184]. Starch is a white, tasteless and odourless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25 % amylose and 75 to 80 % amylopectin by weight. Amylose is a helical polymer made of α -D-glucose units, which are connected to each other through $\alpha(1\rightarrow4)$ glycosidic bonds, see Figure 34 (b). In amylopectin, the glucose units are linked in a linear way with $\alpha(1\rightarrow4)$ glycosidic bonds like in amylose but branching takes place with $\alpha(1\rightarrow6)$ bonds occurring every 24 to 30 glucose units, as shown in Figure 34 (a).

Since starch is a natural energy storage found in many plants, different starch derivatives exist, providing various properties. An abundant starch source is corn. It is part of a lot of food products but is also used in technical applications.

Starch provides several interesting properties, such as polyfunctionality and high chemical reactivity amongst others ^[185]. These properties provide several ways of modifying starch, which in turn offers a variety of material properties ^[186–190]. Physically crosslinked starch shows time-dependent retrogradation, the amorphous structure of the swollen hydrogel regains more structured and crystalline states ^[191,192]. The gel character becomes weaker over time and the desired physiochemical properties change ^[193]. Chemical crosslinks between the chains of the polymer are much more persistent and the gel structure and properties are retained for a long period of time. The formed mesh-network of hydrogels is permeable for water-like liquids, which is an interesting property in many technical applications ^[194–196].

Figure 34. Chemical structure of the starch constituting polymers (a) amylopectin and (b) amylose.

4.5 Flexible Substrates

In printed electronics, flexible devices are often envisaged that reveal further degrees of freedom in the design of the components. PET film is used as a substrate due to its low cost, chemical resistance and printability. The maximum processing temperature of 150 °C is compatible with most functional printing inks. For higher temperatures more expensive polyimide, polyamide or polyethylene naphthalate substrates are available. Paper is also used as a substrate, but offers different properties than polymers. With regard to thermoelectric generators, both electrical and thermal insulation are important, which is why polymeric substrates are reasonable. A feasible way to adjust substrate properties is to use compound films consisting of polymers and metallic foils like Aluminium (Al). Of course, a compromise must be made between flexibility, thermal conductivity and low costs. Usually a symmetric sandwich of polymer-metal-polymer is necessary in order to provide thermal stability, i.e. compensation of the coefficient of thermal expansion (CTE) mismatch. Otherwise problems may arise e.g. curling substrates deriving from heat treatment.

Another approach to the substrate configuration could be the usage of a bulk Al foil and a partially printed thin layer of an electrical insulator covering the areas where the bottom conductor of the TEG is successively printed on. Depending on the foil thickness – the metal layer in a compound foil is around 12 to 25 µm thick – a single Al foil is more difficult to handle than a compound foil due to the reduced stiffness. The thickness of pure Al foils must be higher than that of Al in a compound foil, thus increasing the costs. An advantage of a partially printed metal foil is the possibility of reducing the electrical insulating layer to a minimum, which leads in turn to a reduced minimum thermal resistance.

Compound films as substrates for printed batteries and supercapacitors offer the advantage of a high barrier against environmental influences or loss of the electrolyte. The latter in particular requires good encapsulation of the device so that its function can be guaranteed over a longer period of time. This encapsulation can be achieved by the use of compound material, which in addition to the easily printable and chemically inert outer layers also has an inner layer made of Al as a high-barrier layer.

5 Printed Devices

5.1 Thermoelectric Generators

In literature ^[197–199] there are different approaches to printing thermoelectric generators which can be categorised into the lateral and the vertical design, see Figure 35. The lateral design is realised by printing the thermoelectric materials in just one plane (a). The vertical design requires a reasonable height of the printed structures and may consist of five successively printed layers, Figure 35 (b), or less complex and with only one thermoelectric leg only ^[197], as shown in Figure 35 (c).

Figure 35. (a) Lateral layout printed in one plane ^[198] with temperature gradient parallel to the substrate. (b) Vertical layout with five layers, and (c) vertical layout with only one leg ^[197]. The temperature gradient is perpendicular to the substrate.

Printing in one plane with some overlapping areas, where the different functional pastes are in electrical contact is rather trivial. Problems which may arise with the lateral design are material related. The inks should be compatible regarding their solvents and the surface energies, in order to prevent resolving and to achieve a good wetting on the previously printed layers. The physical application of the lateral design to the heat source/sink is quite difficult, because the axis on which the temperature difference occurs is parallel to the substrate plane. For instance, if printing on single sheets, gathering of these sheets is required and the interconnection of TEGs on these sheets is demanding.

In the vertical version, the temperature difference is perpendicular to the substrate. It is therefore important to deposit thick layers of active material in order to ensure a spatial separation of heat source and sink. Thick layers can be generated from digital data sets using the in vogue 3D printing technology. However, this is usually time-consuming and not efficient for mass production. When relying on conventional printing technology, screen printing shows its advantages, which is also capable of producing thick layers. Although ink layers up to several hundreds of microns are possible, the aspect ratio of height to width is an important criterion. Since this aspect ratio is limited by parameters of printing technology, several layers may be necessary in order to achieve the desired height of the printed structure. Thus, alignment is as crucial as fast curing inks, while keeping the process time in mind. There are graphic arts print products

as well that require more than 20 print runs for a completely printed image. But with costs in mind, the process should be kept as simple as it can be to maintain the benefit of low cost manufacturing.

OTEGO, a spin-off from Karlsruhe Institute of Technology (KIT), has developed a process in which lateral thermocouples are printed on very thin polymer substrates in a continuous roll-to-roll process. A sophisticated concept of folding the substrate results in compact, cube-shaped thermoelectric generators ^[200].

5.2 Supercapacitors

Supercapacitors are electrochemical storage devices for which the operating principle can also be explained by the model of the plate capacitor. This model is based on two electrodes separated by a dielectric. The distance and size of the plates and the material properties of the dielectric, i.e. the dielectric constant, determine the capacitance of the plate capacitor. The structure of the electrochemical double layer capacitor is macroscopically different, but microscopically analogous to the plate capacitor.

At the interface between the solid, negatively charged electrode and the liquid electrolyte, electrons and solvated cations are opposed, or anions are present at the positive charged electrode. The Helmholtz double layer (Figure 8), which forms directly at the phase boundary, now behaves like a plate capacitor. The electrode is separated from the solvated ions only by the solvent of the electrolyte, e.g. water, which is adhering to the electrode. This solvent layer, with a thickness of only a few molecules, corresponds to the dielectric of the conventional plate capacitor. The difference in the nominal capacitances of the components becomes apparent through the different orders of magnitude of the layer thickness of the molecular layer of EDLC solvents and the dielectric in the conventional capacitor. Furthermore, highly porous materials such as activated carbon are used as electrode material in EDLC, so that a very large surface area is available for the formation of the Helmholtz double layer.

The layout of the printed supercapacitor comprises four successively printed layers, see Figure 36, Side View. The current collectors consist of silver ink printed on a PET substrate. The silver layer is covered by an additional carbon-black layer for electrochemical passivation. The third layer is formed by the electrode.

Figure 36. Schematic illustration of the printed supercapacitor arrangement.

The last layer is comprised of the separator and electrolyte, which can be established by using a screen-printable solid electrolyte or a nonwoven soaked in electrolyte. Two strips of the multilayer composite laminated face-to-face form the supercapacitor (Figure 36, Side View).

5.3 Printed Primary Batteries

Printed batteries can basically be divided into two types: the coplanar structure, in which both electrode layers are on the same plane and usually face each other in interdigitating finger structures. And the second variant, in which the electrode areas are stacked on top of each other with the separator layer soaked with electrolyte in between. The coplanar version offers the advantage of applying a printable gel electrolyte over the entire area of the interdigitating fingers. Instead of cell assembly only encapsulation e.g. by lamination is then required. The main disadvantages of the coplanar design are its lower energy density and discharge rates ^[201]. Furthermore, the stacked version is more compact in size.

The main advantageous features of printed batteries are believed to be low cost, the fast manufacturing process, simple processing, a high degree of freedom in designing the battery, flexibility due to thin devices and the ability of fabricating large area devices and series connections of single cells, as shown in Figure 37. Environmental friendliness and non-toxic, disposable materials are also perceived as advantages of printed batteries ^[136]. The main disadvantages are identified as currently high costs due to expensive functional inks, complicated manufacturing methods, and non-optimised printing inks ^[202].

With all the advantages mentioned, however, one must not forget the generally valid disadvantages of printed electronics. An eminently important disadvantage is the necessity of paste optimisation for the respective printing process. As a result, additives are mixed into the electrode pastes, which can be detrimental to the function. The resistance of printed cells to environmental influences is

Figure 37. Series connection of four Zn/MnO₂ cells printed on compound substrate and individual contacts for each cell. The upper and lower rows are folded on top of each other.

just as important as the mechanical stability of the battery module, especially in flexible systems, which must be mastered for reliable operation. The maximum discharge current depends on the good mechanical contact between the components of the printed battery, so that low mechanical compression of the cell causes higher internal resistance resulting in a strong voltage drop with higher current discharge.

The current focus in the research area of printed batteries is on battery design and composition, the optimisation of printing pastes with adjustable rheological and electrochemical properties, and the adaptation of printing technologies. In addition, more efforts are being made to be able to produce secondary cells using printing technology ^[203].

6 Methods

6.1 Preparation of Cornstarch Hydrogels

The experimental procedure for the preparation of cornstarch hydrogels is depicted by Figure 38. Prior to the gelatinisation of the cornstarch hydrogel, the thermoplastic starch powder is made by melt-blending or extrusion. Extrusion allows the control of several parameters but also requires deep process knowledge and sophisticated machines. Melt-blending is possible on laboratory hotplates and thus is an easy and vastly available process.

6.1.1 Heat Induced Reaction of Citric Acid and Cornstarch

Initially, starch filament was prepared via extrusion with Coperion ZSK 18 double screw extruder (Stuttgart, Germany). The extruder barrel length to diameter ratio was 41. The extruder screw was made of conveying, kneading and mixing elements. The design of the screw is the intellectual property of “Institut für Kunststofftechnik”, Stuttgart University, where the tests were performed. In contrast to other reports ^[204–207], only cornstarch and citric acid were used for extrusion without any further chemical as plasticiser, e.g. water or glycerol. The extruder suggests better control over the parameter setting. However, the process volume is rather high, requiring at least 500 g per test run, even with a “small” laboratory extruder.

With the first test run it was obvious that extrusion requires a deep knowledge about processing parameters. The thermoplastic starch obtained by extrusion and melt-blending on a laboratory hotplate was examined by means of Fourier Transform Infrared spectroscopy (FTIR). No significant differences were seen in the FTIR spectra of both thermoplastic starch powders, indicating that both processes provide blends of similar quality and properties. Hence, a much

Figure 38. Experimental procedure: melt-blending of citric acid and starch powders, grinding the bulk thermoplastic starch. Ultrasound sonication of hydrogel mixture and screen printing.

simpler and vastly available process was found in using a laboratory hotplate for melt blending.

Citric acid powder was molten on a laboratory hot plate at 160 °C. Cornstarch powder was added to the liquefied acid and mixed thoroughly. The amount of added starch had to be precisely controlled in order to avoid agglomeration in the melt due to an unfavourable local mixing ratio. The thermoplastic starch was prepared by melt-blending citric acid with cornstarch in a 1:1 proportion. This mixing ratio enables good powder handling and reproducibility of results. After the successful preparation of the resulting solid thermoplastic starch, it was ground again to powder, which was then used as an additive in the production of hydrogels. In Figure 39 the reaction of citric acid with cornstarch is depicted.

Figure 39. Crosslinking of citric acid and cornstarch, created after ^[182] and ^[208].

6.1.2 Gelatinisation of Melt-Blended Cornstarch

It is known that a suspension of water and starch can be gelatinised by thermal or ultrasonic treatment. This physical cross-linking is characterised by entanglement of the polymer chains, hydrogen bonds, hydrophobic interaction and formation of crystallites respectively ^[209]. Chemical modification, i.e. cross-linking, takes place when a reactant such as citric acid is used. In this way, the chemical structure is changed.

The hydrogels were prepared as follows: dry melt-blended acid-starch powder and DI water were added to the mixing container and stirred for few seconds using an ultrasound processor. Cornstarch was added to the suspension. Afterwards, the ultrasound processor Hielscher UP200Ht with a tip diameter

of 7 mm was used for gelation of the mixture. Amplitude was set to 100 % and frequency was 26 kHz. Ultrasound processing was performed in direct contact with the gel, i.e. the sonotrode horn was immersed into the suspension. The end of gelatinisation was indicated by a drop in the applied power, which was accompanied by a remarkable reduction of processing noise, indicating a sudden increase of viscosity. The process was then stopped immediately. The prepared gel was stored at room temperature (23 °C) in glass vials sealed with parafilm. Indirect ultrasound processing was also tested, as reported by ^[210]. However, the so obtained hydrogels showed weaker strength and lower viscosity. Additionally, the processing time was remarkably longer, so that the direct processing was preferred. In addition, the starch granules are supposed to reduce in size when direct ultrasound sonication is used ^[211]. The ultrasound treatment is a combination of cavitation, i.e. massive shearing, and a temperature of approx. 70 °C, deriving from shearing, which leads to a homogeneous hydrogel ^[212]. Moreover, ultrasound treatment leads to increased water absorption in starch ^[213].

6.2 Rheology

“Rheology describes the deformation of a body under the influence of stresses. Bodies‘ [...] can be either solids, liquids, or gases” ^[214].

The term rheology was coined in the 1920s and derives from the Greek aphorism ‘panta rhei’ meaning everything flows. This field of science became more and more important because the rheological properties of materials are decisive for industrial processes such as printing. Materials can be classified according to their behaviour under stress, i.e. shear rate and shear stress.

Liquids like water are ideal Newtonian fluids with shear rates proportional to shear stress. Printing inks in general are pseudoplastic, i.e. shear thinning fluids. Dilatant fluids show the opposite behaviour of shear thickening. Many liquids have both elastic and viscous properties, thus they are named viscoelastic fluids. The flow behaviour of printing inks is a key factor to high quality printing, since the inks need to fulfil several requirements before, during and after the printing process. In the scope of this thesis only the properties of screen printing inks are considered. One of the most important rheological parameters is the viscosity.

6.2.1 Viscosity

The resistance to flow is called viscosity and it is one of the most important rheological parameters not only of printing inks. The dynamic viscosity is a measure of the internal friction of a fluid and is determined from the quotient of shear stress and shear rate.

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (18)$$

with viscosity η in Pa·s, shear stress τ in Pa and shear rate $\dot{\gamma}$ in s⁻¹.

Figure 40. Parallel plate model illustrating viscosity.

Using a simple model, the shear rate and shear stress can be illustrated as follows: Two adjacent, parallel plates enclose a liquid, see Figure 40. By moving the top plate parallel to the bottom plate with the velocity v of the shear force F , laminar shearing will take place in the liquid. The boundary layer beneath the top plate also moves with velocity $v=\max$, while the boundary layer upon the bottom layer does not move at all. The liquid could be seen as being a huge number of infinitesimal thin laminar layers in between these two extreme values. All the layers have different velocities. A linear velocity gradient will be established.

The shear stress τ in Pascal is defined as the force F in Newton (N) applied on the cross-sectional area A in m² of the top plate in contact with the liquid

$$\tau = \frac{F}{A} \quad (19)$$

The shear rate $\dot{\gamma}$ in s⁻¹ is defined as

$$\dot{\gamma} = \frac{v}{h} \quad (20)$$

with velocity v in m·s⁻¹ and the height h in m.

6.2.2 Linear Viscoelastic Regime

Oscillatory measurements provide information about the material under test e.g. linear viscoelastic region (LVR), gel point, flow point etc. and allow categorising the substance in material classes i.e. the type of complex fluid ^[215–217]. The oscillatory measurement is based on an applied sinusoidal strain γ at an angular frequency ω .

$$\gamma = \gamma_0 \cdot \sin(\omega t) \quad (21)$$

The response is the steady sinusoidal stress δ

$$\delta = \gamma_0(G'(\omega) \cdot \sin(\omega t) + G''(\omega) \cdot \cos(\omega t)) \quad (22)$$

In addition to the storage and loss modulus G' and G'' , which represent the elastic and viscous properties of the investigated material, the dynamic viscosity $\eta' = G''/\omega$ and the damping expressed by the loss tangent $\tan\delta = G''/G'$ are determined.

Oscillatory measurements are divided in two regions, the small amplitude oscillatory shear (SAOS) and the large amplitude oscillatory shear (LAOS) regime. The SAOS regime must be chosen carefully in the LVR of the material. With LAOS one leaves the linear region and gains information of the materials structural properties, such as the type of a complex fluid. According to Hyun et al. ^[216] complex fluids can be categorised in at least four types, shown in Figure 41. Polysaccharide based hydrogels in general show Type 3 behaviour. Several rivaling hypotheses for explaining the strain overshoot are discussed in the scientific community ^[218]. An explanation can be found in the concurrently structural breakdown and build-up of weak network structures. The build-up exceeds the breakdown process during the faint strain overshoot.

6.2.3 Thixotropy

Pseudoplastic or shear thinning behaviour describes the reduction of the viscosity while the shear rate increases. If there is a threshold shear rate, which must be exceeded in order to enable the material to flow, it is called yield stress. Pseudoplastic materials are called thixotropic if their pseudoplasticity is time-dependent. In thixotropic materials, the viscosity decreases even at constant shear rates. When no more shear stress is applied, the ink restores, time-dependent, to the initial viscosity value. Thixotropic fluids show specific hysteresis curves depicting the time constant of restoring to the initial viscosity. A partially thixotropic liquid will not recover to the initial viscosity value.

Figure 41. Classification of complex fluids: strain thinning type I, strain hardening type II, weak strain overshoot type III, and strong strain overshoot type IV, according to ^[218].

Figure 42. Schematic of a Michelson interferometer. Through Fast-Fourier-Transformation interferogram is converted into a spectrum

Thixotropy is a major characteristic of screen printing inks ^[219], which are initially highly viscous, e.g. functional printing pastes like carbon black inks. By applying high shear rates with the squeegee and/or the floodbar the ink shows shear thinning that enables the transfer through the mesh openings onto the substrate. Since the ink is still low viscous, the transferred ink layer is able to level and form a smooth ink film. Eventually, the initial viscosity is restored over time ^[220].

6.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a fast analysis technique that provides spectral data mostly between 700 and 4000 cm^{-1} . FTIR uses a broadband radiation source that contains the entire spectrum of wavelengths, so that each wavelength is recorded at once. This is in contrast to dispersive infrared technique, which emits monochromatic electromagnetic radiation at a certain wavelength. As such, FTIR is faster and delivers a higher signal-to-noise ratio, since multiple scans can be performed in a short time, reducing noise impact.

FTIR spectra plot either the absorbance or the transmittance of the emitted electromagnetic radiation versus the wave number. The wave number is the reciprocal of the wavelength as shown in (23):

$$E = h \cdot \nu = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \tilde{\nu} \quad (23)$$

with the energy of the electromagnetic radiation E , frequency ν in Hz, the Plank's constant $h = 6.626 \times 10^{-34}$ J·s, velocity of the radiation in vacuum c in $\text{m} \cdot \text{s}^{-1}$, wavelength λ in nm and wavenumber $\tilde{\nu}$ in cm^{-1} .

The measurement configuration used in FTIR devices is named Michelson Interferometer. In principle, it contains two mirrors, of which one is moved by a motor and the other is fixed, as shown by Figure 42. According to the position of the mirror, the excitation by the full wavelength spectrum can be transformed

into the response at a particular wavelength. The measured raw data, the interferogram, is Fourier transformed, so that an IR spectrum is obtained ^[221].

Samples must be prepared differently for infrared spectroscopy measurement depending on the type of the specimen. Gases can be used in vacuum gas cuvettes. Liquids as pure substances and in solution are also measured in cuvettes. Solids are usually measured as potassium bromide (KBr) pellets, as suspensions, films or in solution. By using an attenuated total reflection (ATR) unit, most samples can be measured without prior and laborious sample preparation.

With total internal reflection in an ATR unit, an IR beam is fed into a crystal at a particular angle. This beam experiences total reflection at the phase boundaries, at which an evanescent wave is created that extends beyond the ATR element. The penetration depth d_p of this wave is sufficient to stimulate an attached sample to interact with the wave entered at this point, see Figure 43. This interaction can be seen in an absorption spectrum of specific material properties ^[222].

Figure 43. Illustration of the measurement setup of an attenuated total reflection (ATR) spectroscopy, according to ^[223]. The depth of penetration d_p is sufficient to stimulate specimen attached to the crystal.

The greatest advantage of ATR measurement technology is the wide range of materials that can be investigated without special sample preparation. It is able to measure solids and powders as well as liquids and gels.

When characterising substances using infrared spectroscopy, the property of this type of electromagnetic beam is used to set small molecules in rotation and small molecular groups in vibration. Possible motions of the molecules are shown in Figure 44. This excitation is visible in the frequency spectrum. It is possible to identify substances with this method because the energies or frequencies required for excitation are specific for chemical groups and thus characteristic for the respective materials.

Figure 44. Exemplary representations of movements induced by IR radiation ^[224]. (a) symmetric stretching, (b) asymmetric stretching, (c) scissoring, and (d) rocking.

6.4 Thermoelectric Characterisation

The thermoelectric voltage supplied by the printed TEG can be determined by a simple measurement setup. An accurate multimeter with a resolution in the microvolt range is used, due to the small thermovoltage provided per thermocouple and per Kelvin. A heat source and a temperature sensor are also required. In the test setup shown in Figure 45, it is simply assumed that the ambient temperature prevails at the surface of the printed TEG.

Figure 45. Simple measurement setup for estimating the thermoelectric voltage supplied by a printed thermoelectric generator (TEG). Left: schematic illustration, right: actual measurement situation.

Figure 46. Measurement setup for thermoelectric characterisation of the ionic liquid.

This assumption is only a rough approximation, since due to the small dimensions in direct proximity to the Peltier device it is impossible to achieve good thermal insulation. Above all, however, at the beginning of the measurement and when the temperature gradient changes over time, the response of the printed TEG and thus the functionality is evident, so that the test setup is suitable for testing the basic functionality.

The Seebeck coefficient of ionic liquids (IL) was measured at room temperature by alternating the temperature between two lateral electrodes, see Figure 46. The voltage difference between the two electrodes was recorded by a nanovoltmeter and the temperature difference between the two electrodes was

evaluated using two thermocouples. The two gold electrodes that are separated 1 mm apart are evaporated by using a shadow mask. The IL is drop-casted on top of the electrodes. The Seebeck coefficient was extracted from the slope of the linear fitted voltage versus temperature difference curves.

6.5 Electrochemical Characterisation

With electrochemical methods the dependencies between chemical reactions and the electrical current is studied. Either current can be fed into the electrochemical system or conversely, an electrochemical system delivers current. The system changes are observed in both scenarios. In the first case it is referred to as an electrolytic cell and in the second case it is a galvanic cell. As a rule, these processes are associated with redox reactions that take place in the electrochemical cell. With the EDLC, however, only static charges of the electrodes occur. Nevertheless, electrochemical methods are important for the evaluation of supercapacitors in order to investigate the effect of the current/voltage fed into or taken from the system.

An electrochemical cell is made of at least two electrodes that are electrical-ly isolated by a separator containing the ion conducting electrolyte. The reaction, reduction or oxidation, takes place at one electrode, while in the same time the counter reaction takes place at the opposite electrode. It is therefore necessary to examine the entire electrochemical cell or to test individual electrodes against a reference electrode, such as a normal hydrogen electrode or an Ag/AgCl electrode. The devices with which such experiments can be carried out are called potentio-/galvanostats according to their functional principle when voltage or current is controlled.

In Figure 47 a schematic illustration of a potentio-/galvanostat is shown. In this configuration, there are three electrodes, namely the counter electrode (CE), the working electrode (WE), and a reference electrode (RE). At CE a current is injected, which is measured at WE either with the low current path representing

Figure 47. (a) Equivalent circuit diagram of a potentio-/galvanostat for electrochemical characterisation of electrochemical cells, according to [225]. (b) Three electrode setup in an aqueous electrolyte solution.

an operational amplifier in current follower configuration or a high current path with a shunt resistor. The potential is measured between RE and WE ^[225]. CE is normally made of an inert material, such as graphite, Pt or Au. Some reference systems may be used as RE, e.g. Ag/AgCl, of which the exact potential must be known. Reference electrodes are specific, non-polarisable electrodes in which a reaction takes place whose rate, i.e. current, does not influence their potential.

The electrochemical reaction to be investigated occurs at WE. For characterisation of the electrolyte system, an inert material may be used as WE. In the course of this work assembled supercapacitors and batteries were examined. Thus, the common two-electrode setup was applied, in which CE and RE are shorted.

Several electrochemical measurement protocols allow for characterisation of the supercapacitors and batteries. The most often reported value of supercapacitors is the specific capacitance ($\text{F}\cdot\text{g}^{-1}$), but its determination is not as straightforward as it is sometimes presented. In ^[226] the authors discuss the validity of calculated specific capacitance in scientific publications. Cyclic Voltammetry (CV) data allow for determination of the capacitance, but it depends on a myriad of parameters ^[227], which all may influence the accuracy of the calculations, e.g. the shape and the chosen segment of voltammogram ^[228] are important as well as the temperature ^[229]. There are several approaches and equations reported in literature ^[228,230,231]. Foremost, when faradaic processes are present, the calculation or estimation of the capacitance from CV data is rather difficult. However, a reliable method for capacitance and ESR determination is galvanostatic charge/discharge cycling (GCD) ^[232]. Moreover, electrochemical impedance spectroscopy (EIS) allows for characterisation of materials and their interfaces ^[228].

6.5.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is used to extract qualitative information from electrochemical systems in a rather fast measurement that allows conclusions to be drawn about the thermodynamics of the redox reactions taking place and electrochemical reactions or absorption processes. In cyclic voltammetry, the potential of the working electrode is scanned linearly by means of a triangular potential waveform. The triangle waveform is characterised by the limiting potentials E_1 and E_2 as well as the scan rate, e.g. $100 \text{ mV}\cdot\text{s}^{-1}$. A complete cycle is achieved when the sweep starts at E_1 and ends at E_1 after passing potential E_2 . One or more of these cyclic scans are then named cyclic voltammetry ^[233]. While controlling the applied potential, the response of the electrochemical cell is detected by measuring the current. As shown by Figure 48, in the CV-diagram the current is plotted versus the potential. It is sometimes necessary to run through several cycles to obtain the desired knowledge, since information about reaction mechanisms may be revealed by repetitive cycles ^[234]. The experiments showed that the measured EDLC curves were stable after approximately three cycles.

Figure 48. (a) Exemplary representations of cyclic voltammograms. An ideal capacitor is represented by a rectangle. (b) Triangular shaped potential with scan rate in Potential/Timeframe.

6.5.2 Galvanostatic Charge/Discharge Cycling

A valuable method for fully assembled devices is the galvanostatic, i.e. constant current, charge and discharge (GCD) cycling. In contrary to CV, here the current is controlled and the potential limits are set. In the simple form, the charge cycle is finished when the maximum voltage is reached and the discharge cycle begins immediately. It is also possible to hold a particular voltage for a specific period. In the testing of EDLC supercapacitors the ions then are allowed to diffuse even into deep pores, thus creating a larger capacitance.

From GCD measurements the capacitance can be calculated, e.g. using equation (24). In addition, it is possible to calculate the equivalent series resistance (ESR) from the voltage drop, e.g. of the discharge process. When current is drawn from the supercapacitor, the voltage drop (IR_{drop}) occurs immediately. After a short time, the linear capacitive voltage drop begins, which represents the energy consumption in the electrochemical cell by the electronic load. Depending on the shape of the discharge curve, it may be necessary to extrapolate the linear capacitive voltage drop to determine the ESR, see Figure 49 (b).

Figure 49. (a) GCD cycling of a printed supercapacitor. The square wave signal represents the applied constant current, the triangular-like waveform the voltage response. The small image displays the approximated voltage drop by extrapolation.

The IRdrop depends on the drawn current and increases with increasing current density. In the course of this work, EC-Lab software from biologic was used, which allows for analysis of data derived from the measurement protocols of the biologic device. The charge and discharge capacitances are calculated from Galvanostatic Cycling with Potential Limitation (GCPL) as described by equation (24).

$$C = \frac{Q_{ch/disch}}{\Delta E_{WE}} \quad (24)$$

where $Q_{ch/disch}$ in C is the total charge stored or released by the supercapacitor. ΔE_{WE} is the voltage difference in V between the initial and final potential either on charging or discharging process ^[235]. Division of capacitance C in F by the mass of one electrode m in g results in the specific capacitance C_{sp} in $F \cdot g^{-1}$

$$C_{sp} = \frac{C}{m} \quad (25)$$

The specific gravimetric capacitance is an important measure in the field of materials science. If the constraints of the supercapacitor are related to the available electrode area or volume, a volumetric or areal capacitance is more appropriate. For this reason, the areal capacitance is often used as a characteristic value for printed supercapacitors.

The ohmic resistance at the terminals of the electrochemical cell is known as the equivalent series resistance ESR in Ω . It represents the sum of all resistances originating from the current collector, the electrode and the electrolyte. The ESR of a supercapacitor can be determined by means of GCD according to equation (26).

$$ESR = \frac{\Delta E}{2 \cdot I_{ch}/I_{disch}} \quad (26)$$

with potential difference ΔE in V and charge / discharge current I_{ch} and I_{disch} in A.

6.5.3 Electrochemical Impedance Spectroscopy

In electrochemical impedance spectroscopy (EIS), the device under test is subject to a sinusoidal signal, either alternating potential (PEIS, E_t) or alternating current (GEIS, I_t) of small amplitude.

$$E_t = E_0 \cdot \sin(\omega t) \quad (27)$$

or

$$I_t = I_0 \cdot \sin(\omega t) \quad (28)$$

If a potential is applied, the current response of the cell is measured. Ohm's law is also valid for impedance Z in Ω , as depicted by equation (29).

$$Z = \frac{E_t}{I_t} = \frac{E_0 \cdot \sin(\omega t)}{I_0 \cdot \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (29)$$

The current response I_t in A is of the same frequency as the applied voltage signal E_t in V, but shifted in phase ϕ . It is also possible to represent the impedance as a complex number. As such, Z is defined as the electrical resistance R in Ω and the complex reactance X with the imaginary unit j and the phase angle ϕ .

$$Z = |Z|e^{j\phi} = R + jX \quad (30)$$

The reactance stems from the conductive or/and inductive nature of the circuit elements, such that the net impedance is described by the following equations:

$$Z = \sqrt{R^2 + (X_C - X_L)^2} = \sqrt{R^2 + (X_L - X_C)^2} \quad (31)$$

with the capacitive and inductive part of the reactance X_C and X_L respectively

$$X_C = -j \frac{1}{\omega \cdot C} \quad \text{and} \quad X_L = j \cdot \omega \cdot C \quad (32)$$

The Nyquist impedance plot is one way to visualise the measured data by plotting the negative imaginary part of the impedance on the y-axis and the real part on the x-axis. This plot allows for estimating the ohmic resistance of the measured sample by extracting the intercept of the plot with the x-axis. The charge transfer resistance R_{CT} is also visible in this diagram, represented by the second and higher intersection of the curve with the x-axis. If the frequency range covered by the measurement is not sufficient, data fitting can reveal the estimated intersections. This kind of data visualisation is also named Cole-Cole plot.

In the Nyquist Impedance representation of the experimental data the frequency is only displayed indirectly. The Bode diagram shows two curves. One represents the magnitude of the impedance, the other the phase angle. Both curves are plotted versus the frequency. This makes the influence of frequency clear at first glance. Since the impedance measurement extends over a wide frequency range, a logarithmic axis representation with equally weighted decades is necessary. The magnitude of the impedance is also on a log scale. Analysis of

Figure 50. (a) Randles equivalent circuit and (b) simulated result shown as Cole-Cole Plot.

EIS data often requires data fitting according to an equivalent electrical circuit model made of passive elements as resistors, capacitors, and inductors. In addition, there are other components whose physical significance is less tangible, such as constant phase elements (CPEs) or Warburg elements^[236]. Figure 50 (a) shows an equivalent circuit diagram that contains this particular Warburg element. This so-called Randles circuit is a simple model representing processes at the electrochemical interface. In Figure 50 (b) the result of a simulation of this circuit is shown. The semicircle obtained by the high frequency stimulation represents the charge transfer resistance R_{CT} . At lower frequency the Warburg impedance represents a diffusion process indicated by the slope with an angle of approximately 45° ^[236].

6.5.4 Ion Conductivity

The ionic conductivity of the electrolyte affects the performance of supercapacitors^[237] and batteries. It is therefore important to investigate the influence of the salt on the ionic conductivity of the printable separator. It is possible to determine ionic conductivity by electrochemical impedance spectroscopy. The specimens are applied between two opposing stainless steel electrodes. According to^[164] it is necessary to obey a certain ratio between the cross-sectional area of the electrode and the thickness of the specimen under test. Otherwise the relevance of the results may be doubtful. When applying the electrolyte/separator system, it has to be ensured that there are no air inclusions or defects. The intercept of the Nyquist plot with the x-axis, which is representing the real part of the impedance, indicates the resistance R of the electrolyte system. Conductivity can be derived by applying Equation (33)

$$\sigma = \frac{l}{R \cdot A} \quad (33)$$

with σ , l , R and A representing the electrical conductivity in $\text{S} \cdot \text{m}^{-1}$, the length or thickness in m, the resistance in Ω and the cross-sectional area of the ion conductor in m^2 .

6.5.5 Discharge Characteristics of Electrochemical Cells

In Figure 51 (a) and (b) the galvanostatic charge/discharge profiles of an ideal battery and an ideal EDLC are shown. The potential of the supercapacitor depends linearly on the charge/discharge time, while the battery should maintain a specific potential during most of the charge/discharge cycle depending on the electrochemical system, Figure 51 (c).

The energy in an ideal EDLC supercapacitor is obtained by using equation (15), $W = I/2 \cdot C(V_2^2 - V_1^2)$. According to ^[238], this equation applies only to constant capacitance C , which is not strictly met for double layer capacitors. The actually available energy can be determined more accurately with

$$E = \int V(t) \cdot I(t) dt \quad (34)$$

with energy E in Joule or W·s, voltage V in V, and current I in A. Equation (34) also applies to faradaic processes, i.e. batteries. The energy that can be drawn from the battery, however, is limited by the cut-off voltage, which is determined by the load or its battery management system. Accordingly, the integration limits t_0 (before the load is connected) and t_1 (when V =cut-off Voltage) are used. In galvanostatic experiments the drawn current is constant.

$$E = \int_{t_0}^{t_1} V(t) \cdot I(t) dt = I \cdot \int_{t_0}^{t_1} V(t) dt \quad (35)$$

Energy storage devices are commonly rated by their energy density in J·cm⁻³ or the specific energy in J·kg⁻¹.

Figure 51. Charge and discharge profiles of (a) an ideal battery and (b) an ideal EDLC according to ^[25]. (c) shows typical discharge profiles of some cell types (c) taken from ^[239].

7 Conclusion and Outlook

7.1 General Conclusion

Technical screen printing is an established process in many different branches of industry. Despite its lower productivity compared to high-volume printing processes such as gravure and flexo printing, screen printing offers convincing advantages, particularly in the wide viscosity range of the print fluids that can be used, the achievable dry ink film thickness that is well controllable and the sufficiently good resolution of the process. It is therefore not surprising that screen printing is a widely-used process in printed electronics, which often requires thicker layers of functional inks than in graphic printing.

As part of this PhD project, it was important that screen printing offers a process in which both established and exotic functional printing inks can be used. The investigation of energy converters and energy storage devices benefits from quasi 3D screen printing, the multiple superimposition of one and the same structure, which thus builds up vertically. It can be assumed that printed electronics is not a disruptive but a complementary technology to conventional electronics production. One reason for this is the necessity to incorporate the functional materials into a printable liquid, which results in a lower performance of the printed device. The obvious advantages of printed electronics are low tool and material costs, high installed capacity of production machines worldwide, comparatively simple process control and a high degree of industrialisation. In addition, it is possible to manufacture easy disposable, environmentally friendly products.

Electrical energy converters and storage devices can be designed for different applications. Printed on a large scale, both systems can help to ensure sustainable energy production and storage for the supply of modern society. Wind power and photovoltaics already account for a considerable share of the energy mix generated by renewable technologies. But thermoelectric energy conversion can also contribute to improving the overall efficiency of energy production systems, despite its low conversion efficiency. An increase in system efficiency is possible through complementary technologies, such as the concept of tandem thermoelectric-photovoltaic converters. Another field for screen printed energy devices are small autarkic nodes of an all-embracing network that may belong to the Internet of Things (IoT) or the Internet of Everything (IoE). The devices are small in size, but a large number of them must be provided, as countless sensors and actuators have to be supplied with energy. Since a certain proportion of the targeted sensors in the IoT environment require only a rather short service life, this area is ideal for printed electronics.

The latter topic in particular motivates this work. Vertically structured thermoelectric generators and supercapacitors, which can be manufactured with the advantages of screen printing, were addressed. The requirements for both device

classes are partly different, e.g. with regard to the maximum ink film thickness. However, there are also similarities, e.g. in the use of functional inks, which on the one hand must comply with the principles of operation of the devices, but also with the processability in the screen printing process and requirements for environmental compatibility or operation stability.

Several questions arose in the preparatory phase and during the investigation of screen-printed energy converters and energy storage devices. The most important ones are discussed.

- i) *How can we address the contradictory requirement that printing inks must be suitable for the printing process but must not affect the desired functionality? How can we maintain the electronic or ionic conductivity or the Seebeck coefficient as high as possible in these thick layers?*

We demonstrated that it is possible to apply thick ink layers of several types of materials in screen or stencil printing, including thermoelectric semiconductors, ionic thermoelectric polymers, polymer electrolytes and mixed ion-electron conductors. The performance of the liquids strongly depends on the ink formulation. An important aspect in the formation of a functional layer is the modification of the ink to ensure good wetting of the substrate. This helps to achieve good adhesion to the substrate and to avoid pinholes and delamination of the printed layer. In thin ink layers, good adhesion with the substrate partially reduces the horizontal stress that occurs in the layers during drying. For thick layers, the mechanical stress within the film is particularly important as it can lead to cracking. Therefore, in the formulation of printing inks, the amount of binder is decisive for improving the mechanical properties, along with the addition of adhesion promoters or surface tension agents. It is important to know how much the electronic and ionic properties of the energy device deteriorate as a result of the addition of such chemicals.

The solvent must be compatible with the application process. The usage of additives must be well-considered, when negative impact on the functionality may be expected. Generally, the performance of printed materials is lower than that of bulk material that could be used in chemical or physical vapour deposition (CVD or PVD) processes due to the aforementioned materials necessary for the print process.

The extent to which printing inks must be optimised for the particular manufacturing process is worth discussing. On a laboratory scale, the formulations are easier to design, because an ink batch can be prepared for each test series, no pot life has to be observed, as a longer shelf life is not necessary. If the inks are supposed to be used commercially, these aspects have to be considered. It is then important to think about long-term stability and the tendency to sedimentation. The homogeneity of the paste and a good dispersion of the functional particles

even after a longer shelf life are also decisive. The printing inks used in this work, which were not used as supplied by the manufacturer, but were either completely self-formulated or at least adapted by additives to the own requirements, were produced according to the principle of keeping the ink system simple. The aforementioned optimisation required for commercial pastes was disregarded and functionality was given priority. For example, it was always necessary to homogenise the inks with a dissolver before printing, and it was even occasionally advisable to adjust the viscosity by adding further solvents or rheology modifiers.

Even experienced engineers are not able to predict the properties of complex paste formulations with a high degree of reliability, so any additional component risks reducing performance. A compromise must be found between the necessary components such as binder, solvent, functional material and – if absolutely necessary – additive. There is a thin line between creating an easy to process high-quality ink layer and an ink that loses as little of the desired functionality as possible. There is therefore no standard recipe, but in individual cases what must be explored is how much of the chemicals that interfere with the function may be contained in the formulation.

ii) How can it be prevented that the resolution suffers when printing thick layers?

With the approach of reproducing the vertical structures of a conventional TEG in terms of printing technology, requirements are imposed on the ink layer thicknesses that must be achieved in screen printing. Depending on the type of material, thicker layers can be advantageous, which helps to maintain the temperature difference between the hot and cold sides. The layer thicknesses of the thermoelectric legs should be at least 100 μm . These layer thicknesses are not common in the field of printed electronics, so that suitable approaches had to be found for the generation of these structures.

Lessons could be learned from the production of printed Braille dots. The Braille dots must be at least 200 μm high, but have a diameter of 1.6 mm and a distance of 2.5 mm. Especially developed printing inks are used for this purpose. The problems with vertically aligned thermoelectric generators differ from Braille dot printing in that although similar layer thicknesses are required, the slope of the cavities in the insulator or the thermoelectric leg should be very steep. The insulator layer is based on the results of other research groups which, however, did not use printing processes. This layer ensures thermal and electrical insulation of the upper and lower electrodes. In addition, the openings in the insulator layer define the geometric dimensions of the thermoelectric legs. The requirements for the printed insulator are high layer thickness and lateral resolution, so that the area of the cavity is retained and does not shrink during the printing process. This results in requirements for the printing ink, which must

have a high viscosity or low flow behaviour after printing. In addition, the edges of the apertures in the stencil must be of high quality.

Two approaches for creating thick ink layers were investigated: the generation of a maximum ink layer height with only one print run and, alternatively, several print runs of thinner ink layers, which require a fast drying process between the individual print runs. By choosing a coarse screen mesh, a thick layer of ink can be printed. However, the coarse mesh also reduces the structural resolution considerably, so that resolution limits are quickly reached with this approach. In the thermoelectric generators of paper I-III, coarse and medium coarse meshes were used. The cavities in the insulator layer have been significantly reduced with multiple print runs. In the course of the thesis, it was shown that multiple print runs with a mesh of high resolution possibly makes more sense.

In the investigation of the ionic thermoelectric supercapacitors, a high-resolution stainless steel mesh was used which, however, also offered a high open mesh area percentage. This allows the targeted layer thickness of over 100 μm to be achieved with seven successively printed layers. The multilayer printed insulator layers investigated in this paper show the potential of screen printing for the generation of quasi 3D structures. To the best of our knowledge, we are the first to have published screen-printed insulator layers with cavities for thermoelectric legs.

In this context, it is also important that the successively printed layers can be cured quickly in the printing machine. An ink that can be cross-linked by means of UV LEDs was available for this purpose. The reduction of the active area of the cavities could thus be reduced to a minimum. For inks that are not UV curable, the multilayer approach may be misleading due to alignment problems when the substrate has to be removed from the machine, e.g. for heat treatment. It was found that stencil printing is an alternative way if the image structures are not complicated. The thermoelectric legs in paper III and V were accordingly stencil printed. This technique is applicable for conventional screen printing inks as well as thermoelectric polymers, polymer electrolyte and mixed ion-conductors.

iii) How can it be ensured that the upper layers do not adversely affect the lower layers when multilayer structures are printed?

The thermoelectric generator requires a bottom and top conducting electrode, typically made of metal, sandwiching the semiconductor or electrolyte. These electrodes are necessary to extract the electricity from the device. While printing a thick pattern of the semiconductor or the electrolyte is the first challenge, the deposition of a top metal layer from a metal paste/ink is another challenge. It is of utmost importance for the function of the vertically structured thermoelectric generators that the upper electrode establishes good contact between the thermoelectric legs on the one hand and does not affect the underlying layers on the other. In fact, there is a risk that the metal ink will actually penetrate the semiconduc-

tor or electrolyte layer and create electrical short-circuits between the two electrodes that would destroy the device.

The re-dissolving of the underlying layer can result in short-circuits between the upper and lower electrode. This makes at least the affected pair of legs unusable. If the cavity is insufficiently filled, such a short-circuit can also occur with the same consequences for the functionality. Especially when printing PEDOT:PSS, sufficient filling of the cavity is critical, as the paste optimised for screen printing with a solids content of only 2% by weight produces only a small ink layer thickness. If the upper electrode is printed on this thin ink layer, the electrode is susceptible to cracking due to the large vertical distances created by the cavities. In addition, the assumed performance of the thermoelectric generator is reduced by the insufficient leg height. This results in a lower temperature difference between the hot and cold side. Due to the possibly higher layer thickness of the metallic conductor, its physical properties dominate in this situation.

In contrast to PEDOT:PSS, it is easier to fill even deep cavities with ionic gels (Paper V). However, there are problems assumed with the diffusion of the upper electrode material into the thermoelectric material. In order to enable printing on the thermoelectric legs, it is probably advantageous if the gels have a high degree of crosslinking. This prevents the solvents of the conductive paste from the upper electrode from dissolving the legs. Negative effects of the printed layers cannot be ruled out with printed energy storage devices either. Both the printed batteries and the supercapacitors use water-based electrode pastes which can be affected by the also aqueous gel polymer electrolyte. Consequences may be delamination or partial detachment of the electrodes. The electrode pastes contain only a small amount of binder. Adhesion and cohesion may not be sufficient in individual cases.

7.2 Conclusion of the Papers

In **Paper I**, the structuring possibilities of screen printing were investigated. The production of thick ink layers is an important criterion for realising vertically structured thermoelectric generators in printing technology. The investigations in **Paper I** were accordingly designed to evaluate the parameters influencing the achievable dry film thickness. The specified goal of achieving a dry ink film thickness of $\sim 100\ \mu\text{m}$ with only a single printing stroke was achieved by using a coarse screen mesh with a mesh count of 18 threads per cm and a thread diameter of $180\ \mu\text{m}$ (18-180) coated with POLYCOL S 295 HV emulsion from Kiwo and a round shaped squeegee. Furthermore, the dependence of the profile of the printed structure on its geometric dimensions was shown. Dome-like profiles with up to a 2 mm structure width could be produced.

In **Paper II**, the insulating layer of the screen printed vertically structured thermoelectric generator was addressed. The insulator layer has a double function. Firstly, the layer provides thermal and electrical insulation. In addition, it

also defines the dimensions of the thermoelectric legs that are applied into the cavities. High layer thicknesses can be achieved by printing the same structure several times in successive printing steps. In this case, the open area is also reduced. In general, there is a reduction in open cavities when multiple layers are printed or when ink flows significantly after printing. Depending on the procedure, this reduction can be very large. Furthermore, the reduction depends on the combination of the printed structure width and the used screen mesh. In data preparation, the reduction of the aperture width can be compensated for to a certain extent by introducing a correction factor. For instance, a correction factor of 1.3 was determined with a 54-64 mesh and a cavity distance of 0.25 mm.

In **Paper III**, filling of the cavities was investigated using two model inks with thermoelectric properties. PEDOT:PSS and self-made nickel ink were used. Both inks do not provide exceptional thermoelectric efficiency, but are well suited for the evaluation of the process. The inks differ in their solids content, which is approximately 2 wt% for PEDOT:PSS and up to 80 wt% for metal particle filled pastes. The filling results are accordingly different. The cavities with a target height of 100 μm must be sufficiently filled to ensure functionality of the thermoelectric generator. Various nickel ink formulations were examined in order to improve the flow behaviour. The original nickel ink formulation achieved an unfavourable ink layer profile. It was difficult to print a silver ink conductor on top of it. By using a full-factorial design of experiments, a formulation was found that is more suitable for filling the cavities.

In **Paper IV**, a mathematical model for estimating the performance of printed thermoelectric generators was developed. In contrast to conventional manufacturing processes, the structural dimensions of printed thermoelectric generators can be easily modified. This degree of freedom was included in the model. The model allows the calculation of two scenarios. On the one hand, the relevant electrical parameters can be calculated from given parameters such as the materials used and the dimensions of the thermocouples. On the other hand, the geometric properties of the generator can be calculated based on the electrical requirements to be fulfilled.

In **Paper V**, ionic thermoelectric materials were applied by screen and stencil printing in vertically structured thermoelectric generators, which were optimised in **Paper I-III**. We are the first to publish screen and stencil printed ionic thermoelectric supercapacitors (ITESCs). Although the theoretical values were not reached, this manufacturing process showed great potential. The difficulty in printing the ion gel arose from the necessity to use acetone as a solvent. Compared to mixtures with other solvents, the gel containing acetone shows reproducible thermoelectric properties. Thus, the acetone could not easily be replaced by another solvent that is compatible with screen printing. However, it was possible to apply the thermoelectric legs using stencil printing instead of

screen printing. If the gel formulation is adapted to stencil printing, this process is promising.

In **Paper VI**, the creation of an environmentally friendly hydrogel is described that is easy to produce and dispose of and can be used as a separator in printed supercapacitors and batteries. The hydrogel based on cornstarch is characterised by good stability and mould resistance. Citric acid is used for chemical modification of cornstarch. The high proportion of acid ensures that it also acts as an electrolyte. Therefore the hydrogel can be used without further addition of an electrolyte as screen-printable gel polymer electrolyte. Prototypes made from screen-printed activated carbon electrodes and gel polymer electrolytes in stencil printing showed comparable electrochemical properties with similar systems published elsewhere.

In **Paper VII**, selected parameters were investigated that are assumed to have a significant influence on the capacity of a printed Zn/MnO₂ cell. Besides the active area, the electrode paste formulation and the concentration and amount of electrolyte, we also investigated the difference between a nonwoven and a hydrogel separator. The gel polymer electrolyte consists of cornstarch modified with lactic acid. The printed cells produced with gel polymer electrolyte showed good performance, but lack in chemical and mechanical stability. With nonwoven separator and optimised electrolyte quantity and concentration, printed batteries were produced with a performance comparable to alkaline button cells.

7.3 Outlook

We see great potential in ionic thermoelectric supercapacitors (ITESC) consisting of ion gels as thermoelectric material applied in screen-printed vertical structures. This device combines the high Seebeck coefficient of ionic conductors and the 3D-structuring of thermoelectric generators (TEGs) by means of screen and stencil printing. We introduced screen printed thick insulating layers containing cavities for thermoelectric legs. The initially used model substances PEDOT:PSS and nickel ink, which were used in the investigation of screen printing of the vertical design, were replaced by ionic gels, so that the performance of the device was significantly increased. It is a great success that we were the first to produce an ionic thermoelectric supercapacitor in screen and stencil printing. And although the printed devices do not reach the theoretical parameters completely, the prototype shows great potential for further investigation. We assume that problems with the complete filling of the cavities and the contacting of the leg materials through the upper electrode may be responsible for the deviation. It is worthwhile to investigate the interaction of the solvents of the upper connecting conductor with the ionic gel in further work. For the future, it would be desirable to use a solvent in the ionic gels that is more suitable for screen printing. For instance, the addition of a solvent with a higher boiling point could improve processability.

While optimising screen printing of vertically structured thermoelectric generators, different approaches to the creation of the insulating layer were examined. High ink layers with just one print run were established with coarse screen meshes. However, these offer only a low resolution. Printing of several layers with moderate ink layer thickness at high resolution was realised using stainless steel meshes. Due to the small thread diameter the open area of stainless steel mesh is larger than that of most of the PET meshes. As has been demonstrated by experience with PET mesh, it would also make sense to optimise the stencil on stainless steel mesh. In accordance with the work in Paper I, the effects of the type and thickness of the stencil on the achievable ink film thickness and structure resolution must also be investigated for stainless steel meshes.

The key for creating thick ink layers by means of multiple printed layers is the fast curing of the individual layer without removing the substrate from the printing machine. The developed UV-LED curing unit was a simple construction that may be improved by implementation of a more complex lamp design, e.g. using higher power UV LEDs and a control loop to measure and control the applied light energy. The latter would increase the reproducibility of the results.

The novel hydrogel separators based on citric and lactic acid modified cornstarch also show potential for practical use in printed functional layers. The positive properties of these gels are the non-toxicity, the good environmental compatibility of the starting materials and thus of the hydrogel itself, good pro-

cessability in screen and stencil printing, the electrochemical performance comparable with similar systems and the availability of the starting materials as well as the simple process of producing the gel. After the investigation of the basic applicability of the gel polymer electrolytes in supercapacitors and batteries, further properties of the gels have to be investigated. Possible aspects of investigation include the reproducibility of the gel properties, the long-term stability in the mentioned devices and the integration of the gels into a stable production process.

The electrodes of the supercapacitors and the printed battery cells contained only a small amount of binders, as it was anticipated that the addition of other additives commonly used in screen printing could impair their function. As a consequence, the electrode ink was formulated under the premise of keeping the recipe as simple as possible. Following this principle, a minimum binder concentration was used and additives e.g. required for preventing sedimentation were deliberately avoided. Now that the principle functionality of the cornstarch hydrogel was shown, the electrode recipe may be optimised in order to provide better mechanical resistance and an improved compatibility of the electrode with the aqueous gel polymer electrolyte or hydrogel. Furthermore, the addition of a non-aqueous electrolyte may increase the performance of the supercapacitors due to a wider operating voltage window and lower susceptibility to desiccation of the gel polymer electrolyte.

8 References

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