Development of 2D and 3D structured textile batteries processing conductive material with Tailored Fiber Placement (TFP)

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Abstract. In recent years smart textiles have gained a significant increase of attention. Electrotherapeutic socks, light emitting dresses or shirts with integrated sensors, having the ability to process data of vital parameters, are just a few examples and the full potential is not yet exhausted. Smart textiles are not only used for clothing purposes. Sensors for the care of the elderly, light applications for home textiles and monitoring systems in the automotive section are promising fields for the future. For all these electrical and electronic features, the supply of power is needed. The most common used power supplies, however, are not flexible, often not lightweight and therefore a huge problem for the integration into textile products. In recent projects, textile-based batteries are being developed. Metal-coated fabrics and yarns (e.g. silver, copper, nickel, zinc) as well as carbon based materials were used to create textile based energy sources. This article gives an overview of textile based electrochemical cells by combining different conductive yarns and a gel-electrolyte. The available materials will be processed by embroidering utilizing tailored fiber placement (TFP). The electrical characteristics of different embroidered patterns and material combinations are examined.

1. Introduction

The interests in smart textiles has increased significantly in the past years and attracted textile designers and technologists in equal measure. Since most of the developed products contain electronic components, they will need a reliable energy source.

Typical energy sources are common rigid batteries or capacitors, as we know for standard electronic devices. Integrating those hard and nonelastic parts into textile fabrics, however, results in the loss of comfort and textile properties. To maintain the drapability, bendability and haptics of those products, several approaches have been made do develop flexible, textile-based energy sources, like capacitors, pseudo-capacitors and also batteries [1]. Batteries and capacitors can be developed directly on textile substrates by coated layer systems [2] and further be integrated into woven or knitted fabrics in the shape of fibers [3-5]. Early approaches have been made with materials similar to common rigid batteries, such as lithium-iron-phosphate and lithium titanate [5]. The approach of using silver electrodes, combined with PEDOT as electrolyte material, is also promising to produce rechargeable batteries [6]. Other researchers pointed out the advantage of carbon nanotubes as electrode material [7].
However, such textile-based batteries usually are not able to match the required energy density and durability as commonly used batteries. Another known problem is the poor reproducibility and reliability of the resulting batteries. Therefore, the dependency of electrode material as copper, silver, and carbon and the amount of iodine-triiodide as electrolyte have been investigated in the past [8]. This report focuses on creating fiber-based batteries via tailored fiber placement to improve the reproducibility. With defined patterns and adjustable parameters, we work on reproducibility and further optimization of 2D and 3D textile batteries.

2. Experimental

2.1. Material overview

The developed batteries consist of two electrodes from different materials and an electrolyte layer across the embroidered yarns. The terminal voltage can be estimated by the redox potential of the two electrode materials. Examples of the potential of materials are $E_{0,Cu} = 0.34$ V for copper, $E_{0,Ag} = 0.79$ V for silver and $E_{0,Ni} = -0.23$ V for nickel. Two electrodes in combination with an electrolyte results in a redox reaction, where the negative terminal (anode) releases ions and the positive terminal (cathode) receiving ions in the process, resulting in a potential difference and an electrical current, if the terminals are connected. The higher the difference of the potentials, the higher the voltage.

Experiments have shown that carbon material is also a well functional partner in combination with copper and silver electrodes. However, carbon does not take place in the redox reaction itself, instead, will act as a pick-up electrode for the reaction between the electrode and electrolyte material [9]. In this research, nickel-, copper- and silver-coated P-phenylene-2,6-benzobisoxazole (PBO) yarns Z-166 with a twist of 4.5 per inch (AmberStrand® by Syscom Advanced Materials Inc.) as well as a carbon yarn, Sigrafil C SBY 70 (Gruschwitz) are utilized. As electrolyte material, iodine-triiodide (KI3), also known as Lugol’s solution, with 1% free iodine (Gatt-Koller) is used.

2.2. Pattern development

Three different patterns have been designed to process the electrode yarns of the battery. The first pattern consists of two parallel cornering lines, with a distance of 2 mm to each other. The proportions of the battery cell are 5.1 cm in width and 5.6 cm in height. The two following samples are designed with meandering lines, of which the first consists of two long parallel lines, yet again with a distance of 2 mm. The dimensions of this pattern are 4.9 cm in width and 5.5 cm in height.

The second meandering pattern consists of 8 pairs of parallel lines, again with a distance of 2 mm between the two materials in one repetition. The next repetitive pair of lines is placed 7 mm next to the previous one. The dimensions of this pattern are 5.6 cm in width and 5.5 in height. The patterns are displayed in Fig. 1.

The patterns have been designed and prepared for the embroidery machine, to process the yarns through the technology of tailored fiber placement, as described in the next paragraph. The stitching length has been set to 1 mm, due to the small size of the batteries as well as for the stability in the curves, to prevent skipped stitches, causing an overlay of yarns, which would result in a short.

Figure 1. Different battery designs: a) sample with 2 parallel cornering lines, b) sample with 2 parallel meandering lines, c) sample with 8 pairs of meandering lines
2.3. Electrode processing
The patterns are fabricated with a ZSK technical embroidery system with a special single needle embroidery head (W-head). TFP is an excellent method for a reproducible and automated embroidering process with gentle treatment of the positioned functional material. The conductive yarns are supplied and placed by a wire and fiber system with a thread guiding element and sewn onto the carrier material with a double lockstitch. The carrier material is fixed and moved by a mechanical clamping frame.

Various parameters can be configured to ensure the quality of the seam pattern and stability of the applied conductive material. The parameters can be adjusted in small steps of 1/10 mm. This includes the movement of the frame in x- and y-direction during the embroidering process, resulting in a more or less broad zigzag stitch pattern, as well as the swing of the thread guiding system to ensure a safe application of the threads, without damaging and stressing the yarn material during stitching and preventing it from fraying.

![Figure 2. W-head and thread guiding system of embroidering machine for tailored fiber placement](image)

Four different yarns are available for creating the electrodes: nickel-, copper- and silver-coated PBO yarn and a carbon yarn. Combining these materials and the three developed battery patterns, 18 different batteries can be created. Table 1 depicts the possible combinations used for the production of the battery electrodes. Finished samples of the embroidered nickel/copper and copper/silver electrodes are displayed in Fig. 5.

| Material combination for textile batteries |
|-------------------------------------------|
| Nickel / Copper                           |
| Copper / Silver                           |
| Silver / Carbon                           |
| Carbon/ Nickel                            |
| Nickel / Silver                           |
| Copper/ Carbon                            |

Table 1. Material combinations
2.4. Electrolyte layer

As electrolyte, iodine-triiodide (KI$_3$) has been used in the form of a mixture of iodine and potassium iodide in aqueous solution. KI$_3$ has been proven to be more efficient, as well as more skin- and environment friendly than metal salts, such as copper sulphate or nickel sulphate [10].

This electrolyte needs to be applied in a gel form to avoid evaporation and drying, which would result in a reduced ion conductivity of the electrolyte. For the gel-electrodes, commercially available gelatine has been mixed with approx. 25 ml of water and left 15 minutes for swelling, afterwards, mixed with 180 ml of water and 20 ml of aqueous solution of KI$_3$ and slowly heated, until the gelatine was completely dissolved. Instead of a magnetic stirrer, a stirring rod has been used for mixing to prevent air bubbles in the gelled solution.

After a time of pre-polymerization, the electrolyte has been reheated to liquefy it again and poured onto the textile electrodes. Subsequently, the current and voltage of the produced batteries are measured.

3. Results and discussion

It can be clearly seen that the open circuit voltages as well as the short circuit currents differ greatly along the chosen electrode materials and the embroidery pattern. Fig. 4 depicts the measured values of these samples.

The nickel copper electrode combination shows some terminal voltage, but does not deliver any current. During the discharge of the battery, nickel is deposited onto the copper electrode forming a surface alloy, which withstand further redox processes. The same is visible for silver/nickel combinations. Surprisingly, the effect is less visible in the copper/silver cell. In this case, copper is dissolved and could...
be deposited onto the silver electrode, but due to the lesser solubility of copper iodide compared to nickel iodide, it may precipitate on the anode. However, this should also limit the delivered current.

In the carbon based cells a different mechanism can be proposed: The electrochemical iodine/iodide equilibrium is realized on the carbon electrode. Iodine oxidizes the metal electrode, leading to a release of electrons. However, this model is similar to processes in redox flow batteries, except the flowing electrolyte and the lack of a separator. Therefore, the role of the separator is realized by the gel electrolyte to some extent, inhibiting some ion diffusion, which would otherwise force the redox reaction completely to take place at the metal surface without external electron flow. The inhibition of iodine migration in the form of I$_3^-$ has probably the highest contribution to the current delivery of such a system. The higher currents of copper based systems compared to nickel based ones cannot be explained by the given data. Due to the less solubility of copper iodide compared to nickel iodide the opposite effect should be expected. Further investigations are necessary to explain the precipitation behaviour.

It is difficult to interpret the data of the silver carbon combination of electrodes, since the silver electrode is prone to precipitation of silver iodine due to the abundance of iodine ions in the electrolyte. This would render the whole system reasonable static. What is seen in the data can possibly be evoked by the diffusion controlled build-up of silver iodide on the electrode.

Differences of the output current due to different embroidery patterns are probable since a diffusion controlled mechanism is proposed for the carbon based cells. Since the migration of iodine needs to be mitigated in that model, patterns exhibiting a larger distance between the electrodes might deliver higher initial currents. However, time dependent measurement were not conducted in this work, but may give further insight in this proposed model.

The data gives some indication, that pattern b) leads to higher current which would be consistent to the model, because the electrode filaments each form almost closed areas bridged by a larger amount of electrolyte to the other electrode. Pattern a) does not show these areas, since the filaments are embroidered in straight lines resulting in smaller electrode bridges.

Additionally, the yarns were impregnated by liquid KI$_3$ after embroidery. Immediately, the values increased significantly as depicted in Fig. 5.

The measured data shows a significant increase of short circuit currents and terminal voltages. The latter is obvious since the concentration of the oxidizer is locally increased. The potential of cells based on carbon yarns and yarns from metals corresponding to insoluble iodine salts should follow a simple Nernst equation

$$E = E_0 + \frac{RT}{zF} \ln \left( \frac{[I_2]}{[I^-]} \right)$$

**Figure 5.** Measurements of open-circuit voltage (mV) and short-circuit current (µA) for all material combinations and 3 battery patterns after addition of drops of KI$_3$
because the precipitated metal iodide and the metal itself do not contribute to the potential. Therefore, an increase of the iodine concentration in the vicinity of the metal electrode should lead to an increased terminal voltage. Copper/silver combinations do not take advantage of this treatment since both electrodes are susceptible to iodide precipitation. However, nickel/silver combinations also exhibit an increased terminal voltage. The short circuit currents are also increased. The relative amount of current between the carbon based cell-types remains roughly constant, but the silver carbon combination shows a different variation along the embroidery pattern, in this case pattern b) gives lower results. For further insights in that issue, time dependent discharge curves need to be recorded.

4. Conclusion
To conclude, it is shown that textile batteries can be created using metal coated yarns as electrodes, especially in combination with carbon yarns. As electrolyte, iodine-triiodide can be used in gelled and liquid form. Gelling this electrolyte results in a flexible surface for textile applications, which can be used for short times. However, the long term stability has to be further investigated.

The iodine/iodide electrolyte leads to a complex redox systems, especially because the lacking of a separator which makes such cells difficult to understand and to optimize. Future research will focus on further electrolyte materials and different electrode materials to achieve a more stable and efficient power generation. For long-term stability, either encapsulation or addition of stabilizing agents has to be investigated.

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