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Research paper

Silver-based reactive ink for inkjet-printing of conductive lines on textiles

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ABSTRACT

Silver is the material of choice for printed electronics. However, dispersed silver particles can block the fine nozzles of an inkjet print head and after printing the patterns have to be sintered at elevated temperatures to provide high conductivity. In this work we investigated and optimized the printing of a reactive silver ink which contains silver in complexed form, therefore avoiding disadvantages of particle dispersions. After printing the complexed silver is transferred into metallic by evaporating the complexing ligands at 50 °C. The ink contains around 11% silver and has a surface tension of 26 mN m^{-1}. It is stable for at least 1 month at room temperature and for at least 3 months at 2–8 °C. The ink was tested on several substrates and an application on textile is shown. The inkjet printed electronic circuit paths on the fabric withstand washing tests, moisture, and heat as well as crumpling.

1. Introduction

Low cost electronics implemented in textiles can pave the way to a fully new generation of smart products in the fields of healthcare, sport, fashion and safety. Although simple solutions have already found their way into the market, still many problems have to be solved and a lot of progress has to be made to enable the commercial exploitation of such products [1,2]. To produce large volumes at low prices, electronic parts were minimized [3] and connected with conductive yarns [4,5]. The next trend now is the printing of all electronic parts [6–9]. Typically silver is used for printing in form of silver particle inks [10–12]. However, these inks require post-sintering at elevated temperatures. Since substrates like polymer foils or textiles do not withstand high temperatures, there are strategies like to sinter at room temperature via a reaction with sodium chloride (NaCl) [13] or use photonic or IR sintering [14,15].

Inkjet printing is optimal if freedom of design is desired. In combination with roll-to-roll printing [16] it opens the way to mass customization since the process is industrially feasible. However, another difficulty is the handling of inkjet inks containing non-solved particles. The dispersions have to be stable and particles must be small enough to fit through the nozzles without clogging it [17].

To overcome this disadvantage, we developed a printing solution based on a reactive material which contains silver in form of a dissolved complex and is therefore particle free. Another advantage is the low-temperature annealing process: simple evaporation of the complex ligands at temperatures below 100 °C is sufficient for precipitating silver and reducing it to bulk silver for creating conductive patterns.

In this work we have adapted and optimized the formulation of conductive inks to make them usable for inkjet printing. The ink is based on the formulation process for silver based reactive inks reported by Walker et al. [18]. To show the capability and the functionality of the ink, a demonstrator has been designed and fabricated.

2. Experimental

2.1. Preparation of the reactive silver ink

The production of the reactive silver ink was firstly described by Walker and Lewis [18] and was produced by dissolving 1 g silver acetate (from Sigma-Aldrich, ReagentPlus®, 99%) in 2.5 ml ammonium hydroxide (from Sigma-Aldrich, 28.0–30.0% NH3 basis) to form a silver complex after about 20 min at stirring at room temperature. The spontaneous reaction is shown in Scheme 1. Silver acetate is dissolved in aqueous ammonium hydroxide forming intermediate silver oxide which forms the diaminesilver (I) complex with ammonium acetate by addition of excess ammonia.

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$$2\ AgCH_3CO_2 + 2\ NH_4OH \xrightarrow{H_2O} Ag_2O + 2\ NH_4CH_3CO_2 + H_2O$$

$$Ag_2O + 4\ NH_3 + 2\ NH_4CH_3CO_2 + H_2O \xrightarrow{NH_3\ /\ H_2O} 2\ Ag(NH_3)_2CH_3CO_2 + 2\ NH_4OH$$

Scheme 1. Reactive process of the silver complex formation [18].

$$2\ Ag(NH_3)_2CH_3CO_2 + NH_4HCO_2 \xrightarrow{\Delta} 2\ Ag + 5\ NH_3 + 2\ CH_3CO_2H + CO_2 + H_2O$$

Scheme 2. Degradation mechanism: bulk silver is formed and the other products are evaporated [18].

A small amount (~200 μl) of formic acid (from Roth, ≥98%, p.a.) is titrated into the solution to reduce non-complexed silver to metallic silver. These silver particles (slightly greyish solution) can be removed by filtration (0.2 μm PTFE syringe filter) before printing. After deposition of the ink on the substrate the silver complex is decomposed by evaporating the ligands and other ink compounds and reduced by residual formate anions to obtain bulk silver patterns (Scheme 2).

After heating to 50 °C all reactants are evaporated and only pure silver with very high conductivity remains (Fig. 1).

However, the stability of the as-produced silver complex using ammonium (NH_3) ligands is low. Silver particles form within time and after printing, silver forms at the nozzle of the print head due to the evaporation during the jetting. After few minutes, the nozzles are clogged by silver particles. Moreover, using ammonia ligands results in significant bubble formation during annealing. Therefore the ink formulation was optimized to improve the inkjet printability of the material. For that the ammonia ligands were replaced by propyl amine ligands with a higher boiling point of 48 °C to reduce the evaporation at the nozzle and increase stability by dissolving 1.18 g propyl amine (Aldrich, purity ≥ 99%, used as received) in 2.7 g water and mixing it with 1 g silver acetate for by stirring for several minutes Again formic acid is titrated until no more metallic silver is formed which can be filtered out before printing.

Further tests to adjust the ink properties in regard to the requirements of the textile application and the printing of conductive patterns on a woven lyocell fabric with standard textile resin-finish are described in the Results section.

2.2. Inkjetprinting process

Inkjet printing tests were done with the DMP-2800 from Dimatix. A piezo voltage of 14 V was enough for good jetting and a standard waveform (Dimatix model fluid 2) with a maximum jetting frequency of 5 kHz enabled proper drop formation. For this work cartridges with 10 pl drop volume were used. During printing the substrate plate of the printer can be heated to a maximum of 60 °C. For all samples this curing procedure was used, otherwise it is stated.

The ink was printed on different substrates. The demonstrator was printed on a woven lyocell fabric with standard textile resin-finish. This fabric was made from TENCEL®,[1] wood-based cellulose fibers by Lenzing AG. Beside the TENCEL®-textile also Polyethylene terephthalate (PET), polydimethylsiloxane (PDMS), glass (Superfrost™ glass slides from Thermo Fisher), latex (commercial latex labor glove) and an acrylate based coating (IJ176-KK from Tiger Coatings) were used.

2.3. Demonstrator fabrication

To show the functionality of the ink, a demonstrator was designed and fabricated. The reactive silver ink was printed on the pre-treated TENCEL®-textile with a resolution of 2540.00 dpi (10 μm drop space). The pattern is printed in 4 layers to ensure high conductivity. During printing the substrate is heated to 50 °C, no further heat treatment is necessary after printing. The demonstrator features small LEDs, a microcontroller on a snap board with a built-in rechargeable Lithium Polymer battery and female snap connectors (LilyPad Arduino SimpleSnap) and a pulse sensor (Amped) purchased from Sparkfun which can be attached to the textile via snap fasteners. The microcontroller was programmed via the breakout board LilyPad FTDI Basic Breakout - 5 V using the software AVRDUDE from Atmel Corporation. LilyPad LEDs and snaps for the microcontroller board and pulse sensor are sewed to the ends of the conductive lines with an electrically conducting yarn. Then the printed circuit is encapsulated with PDMS (Sylgard 184, Dow Corning). For that, component A (base) was mixed with component B (curing agent) in a 10:1 relation and stirred with a glass stick for several minutes. Air bubbles were removed by centrifugation at 2000 rpm for 4 min. Then the PDMS was left to stand overnight in a refrigerator to increase viscosity to about 4000 mPas (initial value of mixture 3500 mPas). For encapsulation the PDMS was applied with a Pasteur pipette by drop casting about 0.1 ml per cm The PDMS encapsulation was cured for 20 min at 120 °C.

2.4. Characterization and measurements

Surface tension and contact angle (CA) values were collected using a Krüss DSA 100 goniometer. Static sessile drop method was used to measure contact angles. Surface tension (surface free energy) was calculated as interfacial tension (IFT) from the measured contact angles of water, diiodo-methane and ethylene glycol using the Owens-Wendt-Rabel-Kaelble model [19]. For viscosity measurements a vibrating viscometer with a precision of ±3% was used and pH-Values were estimated with pH-Fix Quick-Test-Sticks from Macherey-Nagel.

Conductivity was surveyed via a 4-point-probe station from Lucas Labs connected to a Keithly source meter. The measured resistivity is multiplied with a geometrical factor of 4.5324 to obtain the sheet resistance. Thicknesses of the conducting patterns were obtained from height profiles which were measured with a Bruker Veeco Dektak 150 Stylus profilometer (Bruker Corporation, Billerica, Massachusetts).

The silver particle size distribution after annealing on the substrate (Si) was observed via a ZEISS 1540XB CrossBeam SEM.

3. Results

The reactive silver ink is transparent and no silver particles are present. This is an important advantage for inkjet printing as it will avoid all

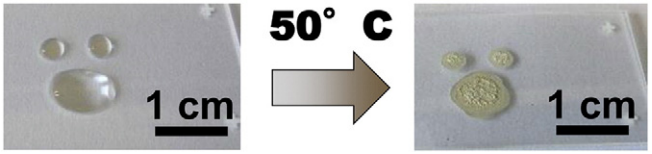

Fig. 1. The transition from the complexed silver ink to metallic silver after heating at 50 °C.

[1] TENCEL® is a registered trademark of Lenzing AG.