

# Particle Based Inks for Inkjet Printing of Thin Catalytic Layers

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## Abstract

*We demonstrate that functional inks can be successfully and systematically formulated to obtain the required properties for printing Fe<sub>2</sub>O<sub>3</sub>-based photoelectrodes. The formulation of the ink as well as the parameters for the printing process can be varied within certain limits to adjust the properties of the electrodes. Characteristics of the formulation process and the printing process are comprehensively studied to estimate the potential of printing different dimensions and structures. For the examination of the photoelectrochemical properties, an optimized photoelectrode is fabricated applying inkjet printing.*

## Introduction

Considering the decreasing resources of fossil fuels, the environmental problems related to their exploitation and the climate problems originating from their combustion, utilizing renewable energy is a critical issue for a sustainable future of our society. Photoinduced water splitting enables the direct storage of solar energy in the form of hydrogen. In the pioneering work of Fujishima and Honda, the technical realization of Photoelectrochemical Cells (PEC) was first demonstrated in 1972 [1].

The Institute of Automation Technology at the Helmut Schmidt University Hamburg and the Helmholtz Centre Geesthacht have joined forces in developing a new approach for the fabrication of photoelectrodes. The inkjet printing process has high flexibility with respect to the spatial structure as well as to the realization of defined surface structures.

The majority of the applications using the inkjet process, which have been explored so far, require layer thicknesses in the range of a few up to several hundred micrometers, e.g. passive electronic components, RFID transponders or bioactive sensors [2]. Considering the photoelectrochemistry of the PEC, absorption length and film resistance restrict the layer thickness (it has been shown that for Fe<sub>2</sub>O<sub>3</sub> target thickness is in the range of 100 to 500 nm [3]). According to theory, the required layer thickness demands solid substance contents of far less than 10 wt. %.

Special challenges concerning the formulation of the functional inks and the printing process arise from the low layer thickness respectively the low solid substance content. The stability of the ink against sedimentation decreases with decreasing solid substance content. Additionally, the formation of inhomogeneous particle deposition patterns increases due to the coffee ring effect [4].

Naturally, the required thickness of the structure cannot be controlled via the number of layers if the printed structure consists of just one single layer. However, formulating the ink, the layer thickness might be controlled by adjusting the solid substance content. With respect to the printing process, layer thickness can be controlled via the spacing of the printed spots and lines. In both cases challenge is to achieve a homogeneous deposition of the particles on the substrate.

An incomplete covering of the substrate may lead to detracting or a failure of the function. Dealing with structures consisting of a single layer, the impact of irregularities in the printing process is high. Hence, with respect to the print layout a conflict arises between a low layer thickness and a complete and homogeneous covering of the substrate.

For the assembly of a PEC electrode, first a particle based ink is developed. The ink has to achieve the requirements with respect to

function, stability and printability. In a following step a single layer is printed with an inkjet printing system. The print layout and signal are controlled, striving to reach the desired geometry. The printed and completely dried electrode is sintered in two steps so the undesired parts of the ink are removed and the catalytic properties of the electrode are adjusted.

## Modeling & Experimental Part

### Material & Apparatus

For the studies concerning the functionality of the ink and the printing process, as well as for the later assembly of the PEC electrode the catalytic active semiconductor iron(III) oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, hematite) is chosen. The particles have a diameter  $D_{50}$  of 30 nm and are purchased from *IoLiTec Ionic Liquids Technologies GmbH, Heilbronn, Germany*. Dispersing agents are the organic solvents butyl diglycol (C<sub>8</sub>H<sub>18</sub>O<sub>3</sub>, BC) and diethylene glycol (C<sub>4</sub>H<sub>10</sub>O<sub>3</sub>, DEG). For ink stabilization ethyl cellulose *Ethocell Std. 7* from *The DOW Chemical Co., Michigan, U.S.* is applied.

For the photoelectrochemical characterization the films were printed on transparent quartz glasses with conducting fluorine doped tin oxide layer (FTO) by *Solaronix*.

The inkjet printing system consists of a print head of the type *MD-K-140* from *Microdrop Technologies GmbH, Norderstedt, Germany* with a nozzle diameter of 70  $\mu$ m mounted in a traversing and positioning unit which was engineered at the Institute of Automation Technology.

### Stability against Coagulation & Sedimentation

To ensure a stable processing of the inks over a longer period, it is necessary to counteract the aging of the inks by proper methods.

The aging of dispersions in terms of coagulation of the particles is caused by attractive respectively repulsive forces on the particle surfaces. A proper way to counteract the tendency for coagulation is therefore the addition of an additive, which encases the particles and affects the molecular surface forces [5].

The sedimentation tendency of dispersions is generally influenced by the viscosity  $\eta$  and the density  $\rho_F$  of the fluid as well as the diameter  $d$  and the density  $\rho_P$  of the particles. The sinking speed of a spherical particle in the case of low Reynolds Numbers (low sinking speed) can be determined using the Stokes equation [6]:

$$v_s = \frac{1}{18} (\rho_P - \rho_F) \frac{gd^2}{\eta}, \quad (1)$$

where  $g$  represents the gravity constant. The diameter of the sedimenting particles is rarely impacted by the process of the ink formulation, nevertheless it may increase due to coagulation during the storage period of the ink. Considering a certain ink system with given dispersion agent and particles the densities are predetermined. Hence, to increase the stability of inks against sedimentation, it is advisable to use as small particles as possible and to avoid the coagulation of the particles. Furthermore it might be helpful to control the viscosity of the ink by using an appropriate additive.

To get insight of the sedimentation and coagulation tendency of particle based inks with low solid substance contents, the influence of a

stabilizing additive on the sedimentation tendency is examined via optical inspection. The viscosity of the inks is measured with a *MCR 301* of *Anton Paar, Graz, Austria* at a shear rate of 6190 1/s and a temperature of 20 °C. Printing tests are performed with a print head of the type *MD-K-140*.

Inks with a solid substance content of 5 wt.% are examined. For this study dispersion medium is the organic solvent BC. The stabilizing additive is ethyl cellulose.

### Coffee Ring Effect

If one wishes to assemble homogeneous structures, an inhomogeneous deposition of the particles on the substrate caused by process inherent disturbances has to be avoided by taking proper actions. A common phenomenon in this regard is the coffee ring effect. This effect is the more developed if the solid substance content is low.

At the moment  $t_1$  of impact on the substrate the particle loaded inkjet droplet takes the shape of a spherical cap due to the surface tension of the fluid phase. The ratio of height to radius and the consequent angle of contact are determined by the surface energy of the substrate as well as the polar and the disperse fraction of the surface tension of the fluid phase. The evaporation ratio is equally in every location of the spot surface, apart from differences due to the temperature. As a result of the proceeding evaporation of the fluid phase, the volume of the drying spot decreases. Due to the surface tension, there is a force that affects the spot and that tries to keep it in the shape of the spherical cap. Additionally, on the substrate surface, there is an adhesion based force directed vice versa. In this manner, the outer edge of the spot is fixed in its position, and at the time  $t_2 > t_1$  the shape differs from the ideal spherical cap. Consequently, the free surface near the top of the spot decreases while the free surface near the substrate increases. In areas with increased free surface the evaporation ratio increases, while it decreases in areas with decreased free surface. A flow is developed within the spot, which runs in the direction of the area with increased evaporation ratio. Thus particles are transported from the center to the edge of the spot. After drying the particles are deposited in the characteristic coffee ring shape.

One can counteract the coffee ring effect by tailoring a marangoni flow in the drying spot. This can be implemented by applying a concentration gradient between the top side of the spot and the area near the substrate by utilizing a binary solvent mixture [7]. The concentration gradient causes a lower surface tension in the area near the substrate and enables thus a marangoni flow directed to the center of the spot.

Within the limits of this paper, it is studied exemplarily to which extent the coffee ring effect of inkjet inks with low solid substance contents can be inhibited by using a binary solvent mixture.

A binary solvent mixture of 70 wt.% BC and 30 wt.% DEG is used; the added fraction of  $\alpha\text{-Fe}_2\text{O}_3$  is 5 wt.%. The content of the stabilizing additive ethyl cellulose is 1 wt.%. For reference, an ink with a dispersion medium consisting of 100 % BC (other characteristics the same as before) is used. The structure of the spot is measured with a digital microscope *VHX-S15* (*Keyence Deutschland GmbH, Neu-Isenburg, Germany*).

### Control of the Applied Amount of Material via the Spot & Line Spacing

The spacing of the single dots and lines as well as the displacement of the lines have a significant influence on the print result of single layer applications. If a high spot respectively line spacing is chosen, the resulting layer height decreases while the probability of gaps in the structure increases due to print errors or the statistical distribution of spot diameters in reality. Smaller spacings lead consequently to higher layers and a higher reliability with respect to the substrate covering. Hence, if the goal is to print thin single layers, a conflict arises between a low layer thickness and complete covering of the substrate.

In first place, a geometrical model for the theoretical layer thickness and substrate covering as function of a dimensionless spot and line spacing is developed. It is assumed, that the dried spots have the shape of spherical caps (this assumption is well fulfilled for dispersion media and substrates developing a sufficient contact angle) and are overlapped additionally (this assumption is approximately fulfilled for small drop deposition frequencies, i.e. the occurrence of coalescence may be neglected). Two adjacent single lines are displaced to each other about the half spot spacing.

This is shown schematically in **Figure 1** for the general case of overlapping single spots (a) and for the case of just not overlapping single spots (b).

The spot and the line spacing are referred to the spot radius

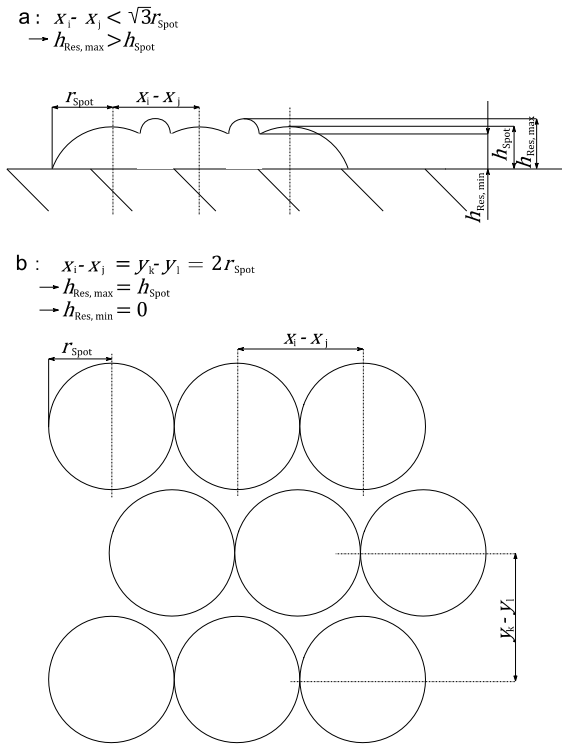
$$\chi = \frac{x_i - x_j}{r_{\text{Spot}}}; \psi = \frac{y_k - y_l}{r_{\text{Spot}}}. \quad (2)$$

$x_{i,j}$  and  $y_{k,l}$  are the coordinates of two adjacent spots in  $x$  respectively  $y$  direction. To enlighten the substrate covering and the layer thickness as function of the applied amount of material, the referred difference between the maximum and the minimum resulting layer thickness is introduced as a parameter describing the homogeneity of the layer

$$\zeta = \frac{h_{\text{Res,max}} - h_{\text{Res,min}}}{h_{\text{Spot}}}. \quad (3)$$

Here  $h_{\text{Res,max}}$  is the resulting maximum layer thickness,  $h_{\text{Res,min}}$  is the resulting minimum layer thickness and  $h_{\text{Spot}}$  is the height of the spot as marked in Figure 1. To determine the applicable parameter area allowing for a print image that enables sufficient thin layers as well as a reliable complete covering of the substrate,  $\zeta$  is plotted against  $\chi$  and  $\psi$ . The spot and the line spacings are varied within single to double spot radius. For validation of the theoretical results later layers with an edge length of 2.8 mm are printed. As before, spot and line spacings are varied within single to double spot radius.

The applied ink has a solid substance content of 5 wt. %, the fraction of the stabilizing additive is 1 wt.%. Dispersion medium is a binary solvent mixture consisting of 70% BC and 30 % DEG.



**Figure 1** Geometrical model for examination of the spot and line spacing of thin single layers

## Control of the Layer Thickness via the Solid Substance Content

The electrical diffusion length is specific for each semiconductor material; in principal it describes the average way that generated charge carriers may travel in a semiconductor before recombination. Accordingly, the thickness of the electrode has to be within the range of the diffusion length so as many of the generated charge carriers as possible can be discharged. At the same time, the layer should be thicker than the inverse of the material specific absorption coefficient. Thus, most of incoming light can be utilized [9].

The height of applications, which allow the printing of several layers, can be controlled via the number of layers. For this is not possible with single layer applications, here the height has to be adjusted in different ways. As described above it is possible to control the amount of applied material via the spot and line pitch. Additionally one can adjust the amount of applied material via the formulation of the ink.

To adjust the height of the structure via the ink, the solid substance content has to be adapted.

Inks with solid substance contents within the range of 20 down to 2.5 wt.% are prepared. Dispersion medium is a binary mixture of 70 % BC and 30 % DEG. The concentration of the stabilizer ethyl cellulose amounts now 2 %. The spacing between two single spots centers is chosen 1.5 times the spot radius; the spacing between two lines is 1 times the spot radius. Two adjacent lines are displaced to each other about 0.5 times the spot spacing. Applying the described inks and print options, quadratic layers with an edge length of 2.8 mm are printed. The resulting layer height is measured with a digital microscope *VHX-S15* after the layer has completely dried. At each location, the height is measured over a distance of 300  $\mu\text{m}$  and the average value is calculated. The height is thereby measured at locations, which are not influenced by edge effects any more. The height is measured at five locations for each printed layer. The average value of these measurements is assumed to represent the height of the accordant layer.

## Assembly of an optimized photo electrode

On the basis of the results of the previous sections, which are dealing with the special challenges that accompanying the inkjet printing of flat thin layers, the properties of the ink and the process can be tuned with regard to the printing of a photoelectrode. With respect to the inkjet printing process the stability against coagulation and sedimentation as well as the reliable printability have to be optimized; with respect to the photoelectrochemistry the demanded layer thickness of about 500 nm has to be realized. By choosing an adequate dispersion media, the homogeneous deposition of the particles on the substrate can be forwarded.

A circle shaped photoelectrode based on  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles is inkjet printed. The diameter of the electrode amounts to 8 mm. The electrode consists of a single layer. Due to the demanded high sintering temperature a FTO coated quartz glass substrate is chosen.

Dispersion media is a mixture of 70 % BC and 30 % DEG. The solid substance content is 5 wt.%, the content of the stabilizing additive is 2 wt.%. The spot spacing is 1.5 times the spot radius, the line spacing is 1 times the spot radius.

In a first step, the printed electrode is sintered for 2 h at a temperature of 300 °C and afterwards for 8 h at a temperature of 500 °C to remove the rest of the solvent mixture and the ethyl cellulose respectively. The heating rate is 10 K/min, afterwards the electrode is cooled down to ambient temperature. To increase the coating adhesion strength and to adjust the photoelectrochemical properties, the electrode is heated up to 800 °C with 10 K/min in a second step, this peak temperature is hold for 20 min.

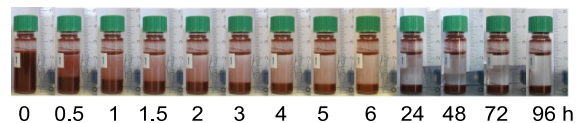
Electrochemical measurements of the electrodes prepared by ink jet printing were performed in a three-electrode *Zahner* PECC cell, controlled by a *Zahner Zennium* electrochemical workstation. The films were contacted as working electrodes. A platinum wire was used as a counter electrode and an Ag/AgCl reference electrode (+ 209 mV vs NHE) for measurements in alkaline medium (1 M KOH). The hematite electrodes were cycled at 10 mV/s under anodic conditions to 0.8 V(NHE) until the cyclic voltammogram (CV) curve showed steady state characteristics. For CVs under dark conditions and illumination were performed. The sample

was illuminated through a quartz glass window (0.5  $\text{cm}^2$ ) using a *LOT* solar simulator (Xe arc lamp, with AM1.5G filter, 1000  $\text{W}/\text{m}^2$ ).

## Results and Discussion

### Stability against Coagulation & Sedimentation

In **Figure 2** the sedimentation behavior of a particle loaded ink without stabilizing additive (ink 1) is shown in the time range of 4 days.



**Figure 2** Particle loaded ink without stabilizing additive, monitored over 96 h

A sedimentation front which is proceeding with time is observable, after about 5 hours the ink has set up a steady state sediment. In **Figure 3** an ink with the same solid substance content is shown after a storage time of two weeks without further mechanical stabilization. The content of the stabilizing additive ethyl cellulose is 2 wt. % (left, ink 3) respectively 1 wt. % (right, ink 2).



**Figure 3** particle loaded inks with stabilizer ethyl cellulose stored for 2 weeks  
left: 2 wt. %                      right: 1 wt. %

While in the case of ink 2 there is already a visible sedimentation front, the particles of ink 3 seem to be homogeneously distributed over the entire height of the sample.

The observed diverging sinking speed of ink 1 on the one hand and ink 2 respectively ink 3 on the other hand cannot be explained solely with the increased viscosity. According to equation 1, the sinking speed depends linear on the viscosity. The viscosities of the inks are measured at a temperature of 20 °C and a shear rate of 6190 1/s. For ink 1, a viscosity of 6 mPa s is measured, ink 2 has a viscosity of 11.1 mPa s and ink 3 a viscosity of 19.7 mPa s.

In fact, most likely coagulation occurs at ink 1 so the effective diameter is enlarged and the sedimentation is forwarded. In the case of ink 2 and ink 3 the coagulation is inhibited by the stabilizing additive.

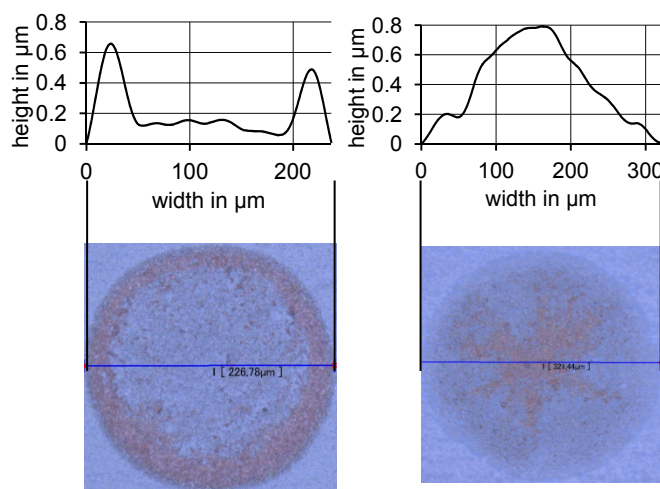
Additional printing tests show, that after a few minutes in the case of ink 1 the forming of a stable droplet is not possible any more. In contrast to that ink 2 and ink 3 can be printed stable within the time range of hours.

Only ink 3 turns out to be able to be storable for two weeks without further mechanical stabilization.

It is shown, that particle loaded inks with low solid substance contents, as required for the printing of PEC electrodes, can be successfully stabilized by adding an appropriate additive in the appropriate ratio.

### Coffee Ring Effect

In **Figure 4**, inkjet printed spots are shown. The ink used for the left spot was prepared with a dispersion media consisting of 100 % BC. The right spot's ink is based on a mixture of 70 % BC and 30 % DEG. The shown profiles are exaggerated to make the shape of the spot visible.



**Figure 4** Inkjet printed spots with different dispersion media  
left: 100% BC right: 70% BC, 30% DEG

In the left picture the majority of the particles is deposited on the outer edge of the dried spot. The symptomatic coffee ring shape is developed. However, using the chosen solvent mixture, a much more homogeneous deposition of the particles is achieved; the particles are positioned more in the center of the spot.

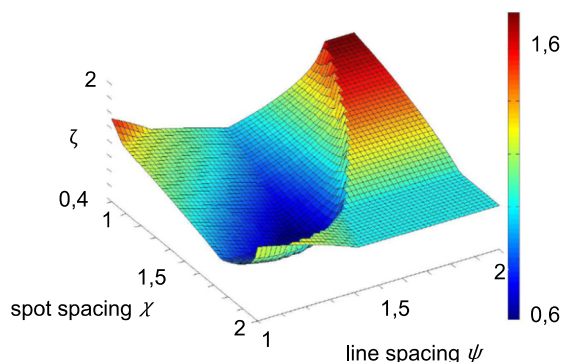
A probable explanation can be derived from the material properties of the components: compared to DEG, BC has the lower surface tension (30 mN/m instead of 44 mN/m). According to theory, in this way a gradient in the surface tension is developed and a marangoni flow is generated. If the marangoni flow is directed to the spot center, one can overcome the internal flow due to the increased vapor ratio on the edge of the spot.

If printing of homogeneous layers is pursued, one has to avoid an inhomogeneous deposition of the particles caused by drying phenomena. It is shown, that the chosen binary solvent mixture inhibits the impact of the coffee ring effect. Thus even using low solid substance content inks, a homogeneous deposition of the particles is achieved.

### Control of the Structure & the Applied Amount of Material via the Spot & Line Spacing

In **Figure 5**, the theoretical height structuring of the layer  $\zeta$  is plotted against the referred spot spacing  $\chi$  and the referred line spacing  $\psi$ . Two adjacent single lines are displaced about the half spot spacing to each other.

In the area of high spot and line spacing, there is a plateau with the value  $\zeta = 1$ . In this zone the single spots do not overlap each other so far that the resulting layer thickness is higher than the spot height (cp. Figure 1). The zones, which are adjacent to the plateau in the direction of the edge of the diagram, mark the areas of incomplete substrate covering, whereas the single spots now do overlap each other so far that the resulting layer thickness becomes higher than the spot height.

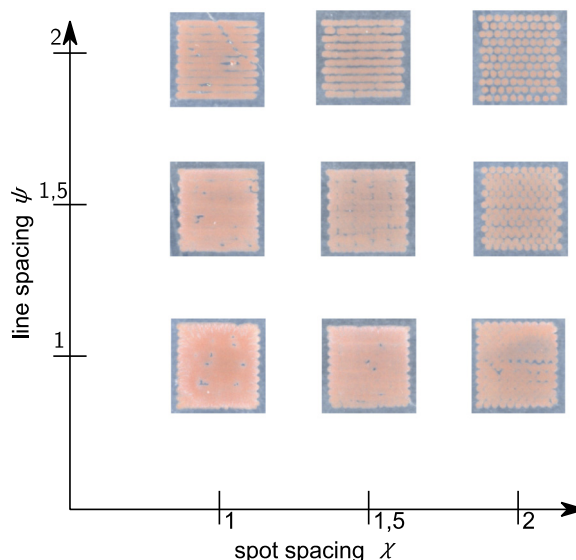


**Figure 5** Theoretical structuring of the layer against the spot and the line spacing

The distinctive border across the diagram, under which the value of  $\zeta$  starts to decrease, marks those combinations of spot and line spacing, which just achieve a complete covering of the substrate. For small spot and line spacings  $\zeta$  rises again and runs towards infinity for the limiting case  $\chi = \psi = 0$ .

If no coalescence occurs, the global minimum of  $\zeta$  marks the point with the lowest structuring. In the case of coalescence the lowest possible amount of applied material and therefore the lowest layer thickness can be found along the characteristic border.

In **Figure 6**, inkjet printed layers with an edge length of 2.8 mm are shown. The layers are printed with selective spot and line spacings according Figure 5. The average spot diameter, which is required to get from the referred values to the print resolution, is determined by experimental means before.



**Figure 6** Inkjet printed layers with varying spot and line spacing

The measured average diameter of the printed single spots amounts to 275  $\mu\text{m}$ . The printed layers consist of 110 (for  $\chi = \psi = 2$ ) up to 420 single spots (for  $\chi = \psi = 1$ ). It becomes apparent that those layers beyond the theoretical limit of an entire substrate covering actually do cover the entire substrate with the exception of single gaps due to unsteadiness in the process. As expected, the number of gaps tends to decrease with decreasing spot and line spacing.

It is shown that the structure of the layer and the amount of applied material can be adjusted via the spot and the line spacing and moreover that a combination can be found that enables a sufficient thin layer as well as a complete covering of the substrate.

### Control of the Layer Thickness via the Solid Substance Content

Figure 7 presents inkjet printed  $\alpha\text{-Fe}_2\text{O}_3$ -layers using inks with different solid substance contents as well as the corresponding measured layer thicknesses.

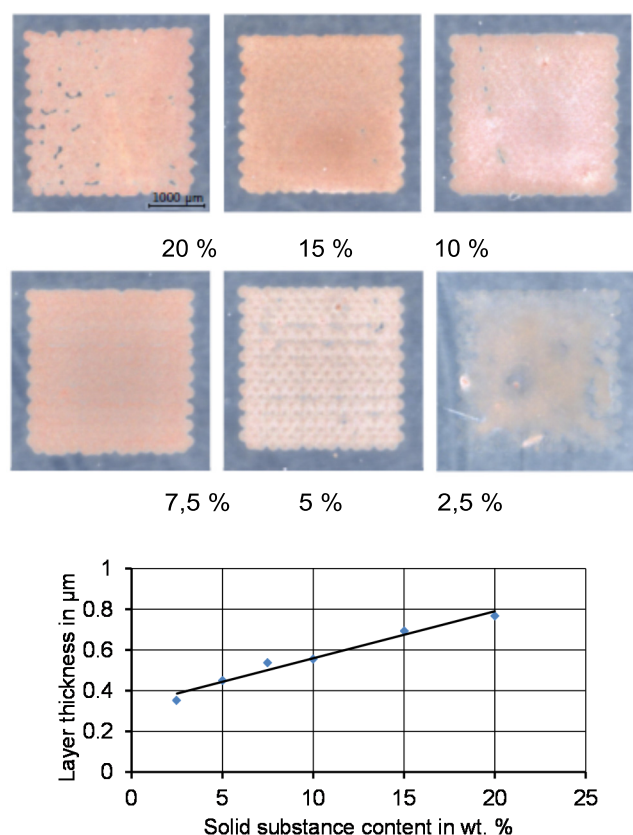


Figure 7 Layers resulting from different solid substance contents and

The inks are stabilized by means of a stabilizing additive and were able to be printed down to a solid substance content of 1 wt. %.

With the exception of single gaps, the layers are almost homogeneously covered; the coloration tends to be brighter with decreasing solid substance contents. Apparently, the layer thickness decreases linear with the solid substance content as expected. Because of the additive, which remains in the layer after printing, the regression line does not run through the origin.

It is shown that the layer thickness can be systematically controlled via the solid substance content. Moreover, it is possible to print layers with the required thickness for the assembly of the PEC electrode in the chosen

model system. However, at a solid substance content of 2.5 wt. % or less the particles do not seem to be distributed homogeneously any more.

### Assembly of an optimized photo electrode

Figure 8 shows an  $\alpha\text{-Fe}_2\text{O}_3$  based inkjet printed and 800  $^{\circ}\text{C}$  peak temperature sintered photoelectrode.

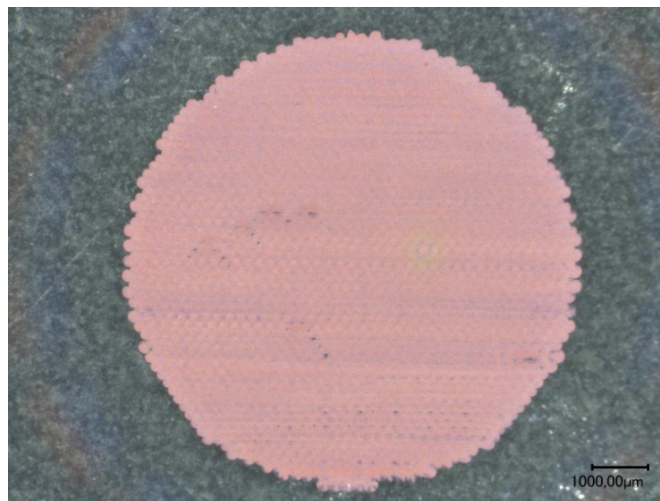


Figure 8 Inkjet printed photoelectrode

The ink was optimized according to the results of the previous sections: by adding the stabilizer ethyl cellulose a stabilization of the ink against sedimentation and coagulation is reached. The utilization of the chosen binary solvent mixture leads to a uniform distribution of the particles on the substrate by means of an inhibition of the coffee ring effect. The applied amount of material is optimized with regard to a complete covering of the substrate; it is controlled via the spot and line spacing. Via the solid substance content the layer thickness is adjusted, the measured mean value amounts to 0.47  $\mu\text{m}$ . The surface of the electrode appears homogeneous, no gaps are visible. The coloring of the electrode after the sintering process shifts towards a darker shade of red.

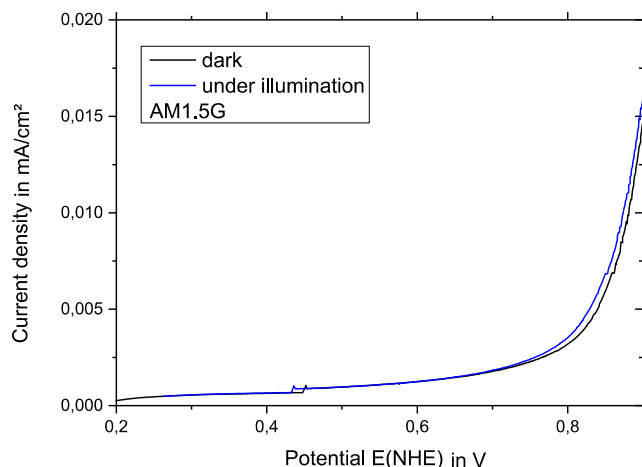
Nevertheless, Raman spectroscopy measurements of the photoelectrode reveal that the fabricated photoelectrode shows the typical characteristics of the hematite. The bulk properties of the semiconductor remain constant after the fabrication.

In photoelectrochemical experiments the fabricated photoelectrode shows low photoelectrochemical activity as depicted in Figure 9. It is assumed that the particle to substrate – contact suffers from low contact. In further experiments an optimized heat treatment procedure for an enhanced electron transfer shall be gained.

### Summary and Outlook

Our results show that it is possible to handle the various demands at the inkjet printing of thin single layers and utilizing low solid substance content inks, using the example of printing PEC electrodes. The demands are studied systematically within this publication.

By means of a stabilizing additive the tendency for coagulation and sedimentation can be inhibited to ensure confident printability. By the selection of an adequate binary solvent mixture a homogeneous distribution of the particles on the substrate with regard to the coffee ring effect is reached. The applied amount of material as well as the covering of the substrate is controlled via the spot and line spacing. The layer thickness, which is especially important with regard to the electrochemical function of the PEC electrode is adjusted via the solid substance content.



**Figure 9** Current density against applied potential

A working photo electrode is successfully fabricated via inkjet printing, the properties of the ink and the process are optimized according to the results of this publication.

Nevertheless the generated photo current is still small. This might be caused by unwanted side reactions or a low contact between the layer and the substrate. A method to increase the purity of the printed electrode as well as an improved heat treatment has to be found in further experiments.

In the future it may be also of interest to investigate the utilization of the advantages of the inkjet printing with regard to the manufacturing of three dimensional geometries. Using a well defined surface geometry, the absorption of light may be enhanced. A defined structuring of the layer itself may lead to an enhanced charge carrier transport within the electrode.

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