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Preparation of Inks for Inkjet Printing of Thin Films in Solid Oxide Fuel Cells

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Abstract

Solid oxide fuel cell technology can achieve high efficiency when producing electric power. To produce these fuel cells with a high quality and a low cost, inkjet printing can be utilized. This technique is highly dependent on having suitable inks for printing.

In this thesis, several inks were made out of spray pyrolyzed $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ which can be used as a cathode material for solid oxide fuel cells. The inks were tested for stability and characterised by electron microscopy and particle size distribution to see if they were suitable for inkjet printing.

Several successful printings were done with an ink which consisted of isopropanol with ethyl cellulose as a dispersant.

This ink appears to be suitable for the purpose of printing cathode layers if the maximum particle size can be controlled.

Sammendrag

For å produsere strøm med høy effektivitet så kan en bruke keramiske brenselceller. For å produsere disse brenselcellene med en høy kvalitet og lav kostnad så kan en bruke blekkskriving. Denne teknikken er avhengig av gode blekk med riktige egenskaper.

I denne diplomoppgaven så ble flere blekk lagd med spraypyrolisert $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, som er et keram som kan brukes som katodemateriale i brenselceller. Disse blekkene ble testet for stabilitet og karakterisert ved bruk av elektronmikroskopi og distribusjon av partikkelstørrelse for å se om de var brukbare for blekkskriving.

Flere utskrifter ble gjort med et blekk bestående av isopropanol og etylcellulose som dispergeringsmiddel.

Dette blekket virker å være brukbart for å skrive katodelag hvis størrelsen til de største partiklene kan bli avgrenset.

Preface

This master thesis constitute the final work of my 5 year Master of Science studies in Material Science. The work has been carried out the Department of Material Science and Engineering at the Norwegian University of Science and Technology (NTNU).

I would to thank my supervisor Hilde Lea Lein for her contributions and good spirit through the final year. I would also thank my co supervisor, technical staff and the ceramics group that I have been a part of for valuable input. There are more people that deserve praises, you know who you are, thanks.

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Introduction

Due to a higher focus on solutions that are more friendly to the climate, solid oxide fuel cells (SOFC) are getting a lot of attention due to their possibility to convert different types of fuel to electrical energy in a very efficient manner. The SOFC is suitable both for large mobile and stationary applications.

One of the challenges with SOFC is in the production of high quality cells in a cheap manner. Several techniques are in use today, and one that is new to the field is inkjet printing. The idea behind using inkjet printing is that it is possible to have a good throughput while at the same time having a highly detailed cell design. Inkjet printing can also be used to reduce cell design time, due to the ease of which one go from design to production of a prototype.

One of the challenges of inkjet printing is to make a stable ink. This have to be done before printing properties can be evaluated, previous work have been focusing both on the properties of the ink and on the properties of the fuel cells created by printing.

1.1 Aim of the work

The aim of this thesis is to investigate the possibility to use inkjet printing to fabricate ceramic layers of spray pyrolyzed $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) from CerPoTech. LSC is a good cathode material for SOFC cells because of its high electrical and oxygen conductivity. A stable ink is to be produced and tested. In the previous project work, two challenges came up. The first was the lack of stability in the solutions. The second was the large particle sizes found in the powder that would be a challenge as they can easily clog the small nozzles. These two challenges have been tried solved.

Chapter 2

Theory

2.1 Inkjet printing

Inkjet printing is basically about precisely placing tiny droplets on a surface by ejecting them from a reservoir. The ejection mechanisms differ, the two types that are commonly used in commercial printers are thermoelectric and piezoelectric, as shown in Fig. 2.1. They both work by creating a pulse in the ink, thus ejecting a droplet. In the thermoelectric design, the pulse is created by rapidly heating and cooling the ink, which forms a gas bubble that collapses and thus creates a pulse. This leads to certain requirements for the ink, as it needs a volatile part to be jetted. In the piezoelectric design, the pulse is created directly through the use of a piezoelectric element. This leads to less requirements for the ink, and thus greater versatility.

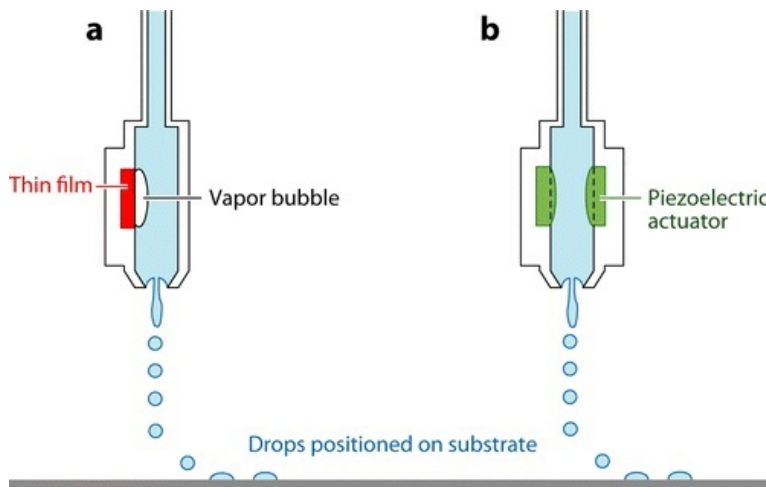


Figure 2.1: Forming of a droplet in a) thermal and b) piezoelectric design. Figure taken from [1].

As the nozzles used in inkjet printing are small, large particles needs to be avoided to prevent clogging. It is stated by I.M. Hutchings and G.D. Martin that the particles should be lower than one tenth of the nozzle diameter, and preferably one fiftieth to avoid blocking the nozzle[2].

2.2 Stabilization of solutions

A solution is stable when it does not change in any way over long periods of time. In this thesis, small ceramic particles are suspended and equally distributed in a solvent. The most common ways for such a solution to destabilize is that the particles either settle and form a sediment due to their high relative density, or agglomerate due to their small size and then settle. The aim when stabilizing a solution is to avoid the agglomeration of particles, which is due to the attractive van der Waals forces in combination with Brownian motion[3]. To counter these attractive forces, repulsive forces from either electrostatic or steric stabilization can be used.

2.2.1 Electrostatic stabilization

Particles submerged in water will develop a charged double layer on the particle. This layer induces a net charge around the particle. When a particle with a similar charge gets close, the particles will repel each other due to the electric charges. These repulsive energies causes the solution to stabilize as the particle won't be able to agglomerate. A measure of these energies is the zeta potential, which can be calculated in experiments. A high absolute zeta potential indicates a stable solution[4].

2.2.2 Steric stabilization

In a sterically stabilized system, molecules are attached to particles, these molecules are polymers of different kinds. They'll have a non-soluble part that attaches to the particle, and a soluble part that is dissolved in the liquid. These long chains results in two different repulsive energies when particles closes in on each other. The first is the osmotic pressure due to the high concentrations of chains in the overlap area. The other arises from the steric repulsion due to overlapping of chains. These forces arise from enthalpy and entropy respectively[3].

2.3 Particle size distribution

The particle size distribution (PSD) of the powders is used in this study to predict stability and to give a clue to whether the particles fit through the nozzles. Laser diffraction can be used to determine the size of particles. This technique uses a laser to illuminate particles, which will then create a diffraction pattern based on the particle size and the refractive indexes of the fluid and the particles. Knowing the indexes, the particle size can be calculated. This works for a wide spectre of particles, from small ones at 10 nm to relatively large ones at 1 mm. While this technique is fast and easy to perform, the analysis relies on the assumptions that the particles are spherical and non porous. For special geometries, this can cause inaccurate results. So, this technology is best used as a supplemental technique for comparison between similar samples[5].

Chapter 3

Experimental work

In the experimental work, there were three areas of focus. The first was to try to stabilize particles by additions of polymers for steric stabilization and adjustment of pH for electrostatic stabilization. The second was to reduce the size of the particles in the ink. This was done either by removing them or breaking them apart. The third was the printing of the ceramic powder with an inkjet printer. The first and second partially overlap, due to smaller particles being easier to stabilize and the unstable large particles can be removed by settling.

3.1 Chemical listing

In table 3.1, all the chemicals used are listed. Not much information is available about Dolacol D 1003, except that it is a purely organic compound that can be entirely removed by heat treatment. The ammonia and nitric acid was taken from student labs due to the small amounts needed, and all except the concentration is unknown for these.

Table 3.1: Chemicals used in the thesis.

| Chemical | Name in text | Producer | Purity/specification |
|--|------------------|--------------------------|--|
| Ammonia, NH ₃ | NH ₃ | N/A | 0.1 M |
| Dolacol D 1003 | Dolacol | Zschimmer & Schwarz GmbH | N/A |
| Ethanol | Ethanol | Kemetyl | 100% |
| Ethyl Cellulose | EC | Sigma Aldrich | Viscosity 10 cP, 5% in toluene/ethanol 80:20 |
| 2-propanol Analar Normapur | Isopropanol | VWR | 100% |
| La _{0.6} Sr _{0.4} CoO ₃ | LSC | CerPoTech | N/A |
| Nitric Acid, HNO ₃ | HNO ₃ | N/A | 0.05 M |
| PolyVinylPyrrolidone | PVP | Alfa Aesar | Avg. M.W. 58'000 |
| Water, Distilled | Water | | 4.5 MΩ cm |

3.2 Equipment used

Some equipment and techniques were used several times in different parts of the thesis, they are listed here, and when referred to, this is the equipment used.

3.2.1 Electron microscopy

All microscopy imaging was done with a Hitachi S-3400N Scanning Electron Microscope (SEM).

3.2.2 Ultrasonic treatment

All ultrasonic treatment was done at a Branson - Digital Sonifier, Model 450 400 W.

3.2.3 Particle size distribution analysis

PSD analysis was done with a Horiba Partica LA-960. All measurements were done with the same carrier liquid as the inks tested, as tests have shown that using another liquid will destabilize the suspensions. The system was flushed once with the carrier liquid before running the measurements. This was done to remove traces of powder and/or liquids from previous samples. When using isopropanol as a carrier liquid, no stabilizers were added. For the samples with 80% water and 20% ethanol, PVP was added in the same ratio as in the sample tested. A transmittance of 85% was aimed for when adding the sample. The settings are shown in table 3.2.

Table 3.2: Refractive indexes and acquisition time settings for PSD measurements.

| Carrier liquid | Refractive index liquid | Refractive index powder | Imaginary refractive index powder | Sample data acquisition times |
|---------------------|-------------------------|-------------------------|-----------------------------------|-------------------------------|
| Isopropanol | 1.378 | 1.700 | 1.000i | 50000 |
| 80:20 Water:Ethanol | 1.333 (water) | 1.700 | 1.000i | 50000 |

3.3 Stabilization

In the project thesis[6], a semi stable dispersion was made out of either isopropanol or alpha-terpineol and ethyl cellulose. In this thesis several more combinations were tried to see whether suspensions with higher stability could be achieved. The focus was not to see how stable a solution was, but to see whether it could compete with EC. There are thus no detailed settling experiments as it was in the project thesis. Electron microscope images of the ink in a wet state were taken to provide a picture of how the particle were dispersed in the ink.

3.3.1 Using pH as stabilization

The zeta-potential of LSC was measured in the Beckman Coulter - Delsa Nano C shown in Fig. 3.1. This system has the capability to automatically measure the zeta potential at different pH values by using an auto titrator to adjust the pH of the solution before each measurement. LSC was first dispersed in water and subjected to a few minutes in an ultrasound bath to break agglomerates, it was then added to the measuring reservoir of the Delsa Nano C where it was thinned out in adequate amounts of distilled water for measurement of the zeta potential. The water/powder ratio was decided by the machine, as it required the particle concentration to be in a certain area, indicated by "counts" on the display. 0.05 M HNO_3 and 0.1 M NH_3 was used in the experiment as an acid and base respectively.

Due to problems with the instrument, the results were only used as a guidance for which areas to test for stability. The first measurement was set to be from pH 7 to pH 3 with a measurement interval of 1. The second measurement was from pH 7 to pH 4, with an interval of 0.5, but this was stopped prematurely due to problems with the instrument. The settings for the second measurement are shown in the appendix, with the same applying to the first measurement, except for the pH values.

Test were run at basic pH values, but these did not give any results at all and were abandoned.

A test was done with pH stabilization in nitric acid. The sample was mixed and then sonified with an ultrasound tip, the content is given in table 3.3.

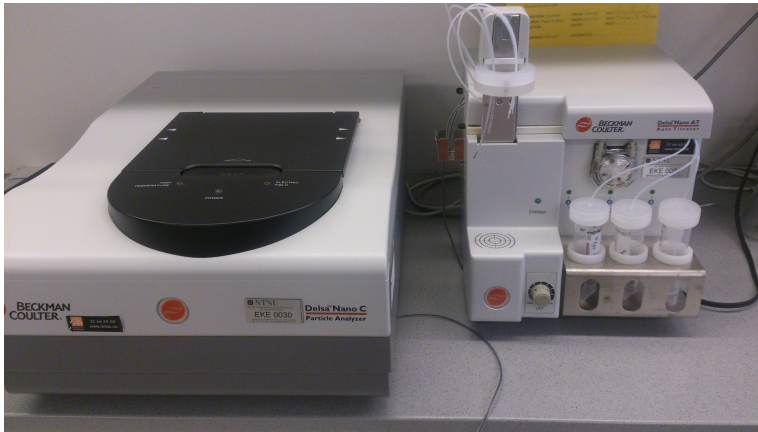


Figure 3.1: Beckman Coulter - Delsa Nano C particle analyzer and auto titrator.

Table 3.3: Contents of pH stability sample.

| HNO ₃ | LSC | Sonification |
|------------------|-------|------------------------|
| 20 ml 0.05 M | 0.8 g | 90 s at 30 % amplitude |

3.3.2 Testing polyvinylpyrrolidone as a stabilizer

An attempt was done to check if the process Esposito et. al.[7] used to make ink out of yttria stabilized zirconia (YSZ) would work for LSC. The polyvinylpyrrolidone (PVP) was added at the same 8 mg m^{-2} of LSC. The surface area of the LSC was estimated to be $16 \text{ m}^2 \text{ g}^{-1}$ from BET analysis during the project work[6]. PVP was dispersed by 53 % by weight in ethanol. This was left for a day to stabilize into a viscous liquid. After this, it was added to the water and the rest of the ethanol in a 250 ml milling jar made from polyethylene. The 5 mm YSZ milling balls were added before the LSC to avoid concentrating powder at the bottom of the jar. Enough balls were added so that they were barely covered with liquid. Batch 1 was left on a U.S. Stoneware mill for 10 days at approximately 125 RPM. While batch 2 was only milled for 8 days at the same speed due to a breakdown of the mill. The exact content of the solutions is shown in table 3.4.

Ultrasound was also tested to disperse and break agglomerates in the solution instead of milling. This was done with an ultrasound tip at 30% amplitude. The procedure is the same as with the milling solutions, but was done in a glass vial.

3.3.3 Testing Dolacol as a stabilizer

Dolacol was tested on its own as a stabilizer. The ratio was based on the ratio Wagner successfully used in his master thesis[8]. This was tested in both ethanol and isopropanol with ultrasound. The solvent and Dolacol were added to 60 mm × 26 mm glass vials. They were then subjected to 90 s treatment with an ultrasound tip at 30% amplitude. The

Table 3.4: Contents of PVP-stabilized solutions, note that this is the total ethanol content, used both to disperse PVP and as a carrier liquid.

| Batch | Water | Ethanol | PVP | LSC | Milling/sonification time |
|-------|-------|---------|--------|---------|---------------------------|
| 1 | 40 g | 10 g | 1.57 g | 12.25 g | 10 days milling |
| 2 | 40 g | 10 g | 0.80 g | 6.25 g | 8 days milling |
| 3 | 16 g | 4 g | 0.63 g | 4.90 g | 60 s sonification |

LSC was then added and subjected to the same treatment to break the heavily agglomerated powder. The exact contents are given in table 3.5. The glass vials were left alone with a lid on for 1-2 days before checking if the solutions were stable.

Table 3.5: Contents of stability measurement samples with Dolacol

| | Ethanol | Isopropanol | Dolacol | LSC |
|----|---------|-------------|---------|-------|
| ED | 20 ml | N/A | 0.16 g | 0.8 g |
| ID | N/A | 20 ml | 0.16 g | 0.8 g |

3.3.4 Wet ink

A QX-102 wet SEM sample holder from Quantomix, seen in Fig. 3.2, was used to image the ink in wet mode. A dispersion with 5 times the LSC and EC content of the "IE" ink in table 3.6. This was left for 18 hours before it was used. The dispersion was added to the sample holder with a plastic pipette. The pressure was set to 30 Pa and the voltage to 25 kV.

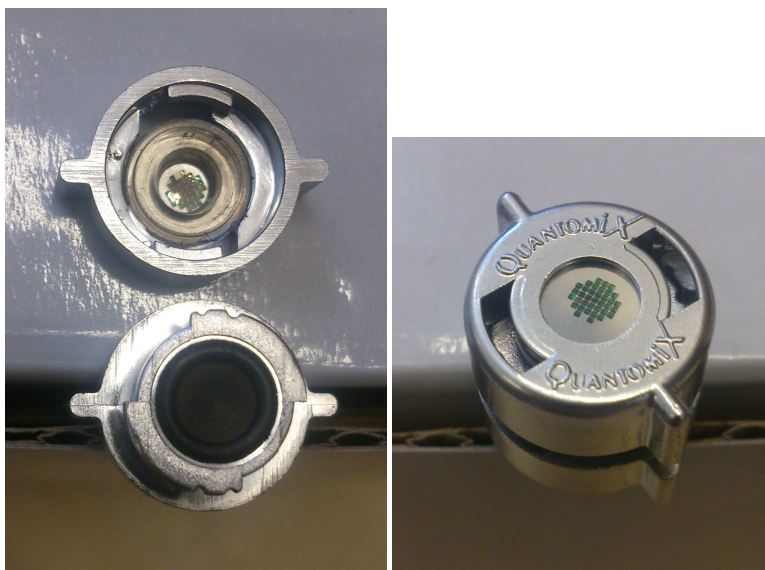


Figure 3.2: The Quantomix QX-102 sample holder

3.4 Size control

Several ways were used to control size: milling, settling and filtering. All of these methods were controlled by particle size distribution measurements.

3.4.1 Preparation of samples for stability measurements

Stability measurements were done in the top layer of the solution to see how the PSD changes over time. The top 30% were chosen because it would be enough to run several measurements and it would give a good indication of the stability of different sizes. Additional measurements were done for the mid 30% and bottom 40% to see how they compared to the top.

When preparing samples for stability measurements, isopropanol was measured up and added to 60 mm × 26 mm glass vials. For samples with Dolacol, the Dolacol was added directly to the isopropanol on a scale. The EC was weighed before being added to the isopropanol. This dispersion was then subjected for ultrasound tip treatment for 90 seconds at 30% to dissolve the EC in an efficient manner. LSC was then added before being subjected to the same ultrasound treatment to break up agglomerates. The exact content is given in table 3.6.

10 ml of sample was then transferred to grad. cylinders for settling. The grad. cylinders were sealed with aluminium foil and Parafilm to reduce evaporation. When taking the sample for PSD, 3 ml of liquid was removed from the top with a plastic pipette. Care was taken to avoid shaking the grad. cylinders. For the 2 day IE sample, an additional 3 ml was taken from the mid and the bottom was decanted out to avoid getting the sediment from the bottom into the sample. PSD on these samples were done after some time, so

Table 3.6: Contents of stability measurement samples

| | Isopropanol | Dolacol | Ethyl Cellulose | LSC |
|-----|-------------|---------|-----------------|-------|
| IDE | 20 ml | 0.16 g | 0.04 g | 0.8 g |
| IE | 20 ml | N/A | 0.04 g | 0.8 g |

they were subjected to ultrasonic treatment for 30 s at 30% amplitude to redisperse and deagglomerate the solutions. The short time was due to small sample size, where excessive ultrasonic treatment would lead to the sample cooking.

3.4.2 Filtration

The size distribution was analysed on filtrated and unfiltrated sample to measure the effectiveness of filtration. A Whatman Puradics 13mm syringe filter with a 2.7 μm pore size was used to filtrate the IDE sample from table 3.6.

3.4.3 Planetary milling of powders

Planetary milling was done on the powder to break new surfaces and reduce particle size. The planetary mill that was used is a Retsch PM 100. The particles were milled in a 125 ml ZrO_2 container with ZrO_2 balls. The specifics for each milling is shown in table 3.7, the content of the solution is the same as the IE sample in table 3.6. Ultrasound was not used to deagglomerate the dispersion.

Table 3.7: Parameters for planetary milling.

| Name | Ball size/amount | Milling RPM/time |
|--------|------------------|------------------|
| PM I | 10mm/25 | 400/30 min. |
| PM II | 5mm/100 | 400/30 min. |
| PM III | 5mm/150 | 400/30 min. |

3.5 Printing

An Epson Stylus Photo R220 with a piezo electric nozzle was acquired. It has an estimated nozzle size of around $18\text{ }\mu\text{m}$, this is not specified by Epson, though a minimum droplet size at 3 pl is specified[9]. This droplet size is used to estimate the nozzle size by assuming a perfect spherical droplet with the same diameter as the nozzle. But the printer can adjust droplet size during printing and it is thus hard to make assumptions. Two empty black cartridges and a chip resetter was bought from inksupply.com. The chip resetter resets the counter that tracks the ink level in the cartridge, and was bought because the printer refuses to print with "empty" cartridges.

Before the first printing with LSC, the standard black ink cartridge was removed and a cartridge filled with ethanol was inserted, the rinsing programme on the printer was run and several black pages were printed to remove all the remaining ink from the system. This was repeated with isopropanol afterwards due to isopropanol being the solvent in the ink. The ethanol cartridge was emptied and flushed with isopropanol before adding the ink. The ink was filtrated through a Whatman Puradics 13mm syringe filter with a $2.7\text{ }\mu\text{m}$ pore size to avoid large particles. The different types of ink used in the different printings are shown in table 3.8, and the procedure is the same as for the stability measurements.

The printing was done in black and white mode where black and white pictures were printed. The printing was done rapidly to avoid that the unstable ink would settle and cause problems. After each printing session, the LSC ink cartridge was removed and flushed with isopropanol, and a cartridge with isopropanol was inserted and used to rinse the printer by printing and using the rinsing program.

Table 3.8: Content of printed inks.

| # | Isopropanol | Dolaccol | Ethyl cellulose | LSC | Ultrasound treatment | Other |
|---|-------------|----------|-----------------|-------|----------------------|------------------|
| 1 | 20 ml | 0.16 g | 0.04 g | 0.8 g | 90 s at 30% | Fresh |
| 2 | 20 ml | 0.16 g | 0.04 g | 0.8 g | 90 s at 30% | Settled, 17 days |
| 3 | 20 ml | N/A | 0.04 g | 0.8 g | 90 s at 30% | Settled, 4 days |

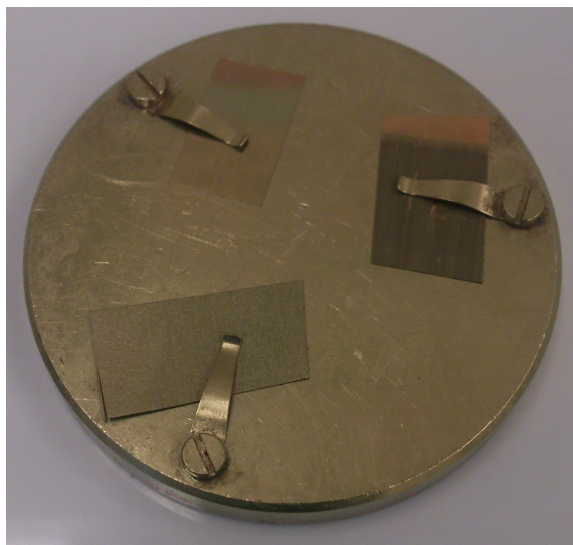
Several printouts were made. Ink #1 was used to print on paper only to see whether it was possible for the printer to dispense the ink. Ink #2 was used on paper to see how diluted the ink was after long storage and on a polyester film to see if it was printable on level surface with different wetting properties than paper. Ink #3 was only used on the polyester film to produce samples for electron microscopy. All printings were done in one layer, except for one in the last batch of polyester prints. This was a 4 layer print, with a 30 second drying time in between each layer.

3.5.1 Electron microscopy of printed ink

The printed samples given in table 3.9, were placed on the sample holder shown in Fig. 3.3 and coated with gold using an Edwards Sputter Coater S150B. The current was 20 mA and the sputtering time was set to 2 minutes.

Table 3.9: The samples used in SEM imaging

| Ink # | Substrate | No. of prints |
|-------|-----------|---------------|
| 1 | Paper | 1 |
| 3 | Polyester | 1 |
| 3 | Polyester | 4 |

**Figure 3.3:** The sample holder with samples after coating.

Results

4.1 Stabilization

4.1.1 Using pH as stabilization

The results of the zeta potential measurements in Fig. 4.1 shows that the zeta potential increases with lower pH values. It is hard to say anything about the reliability of the results because of the technical problems with the equipment.

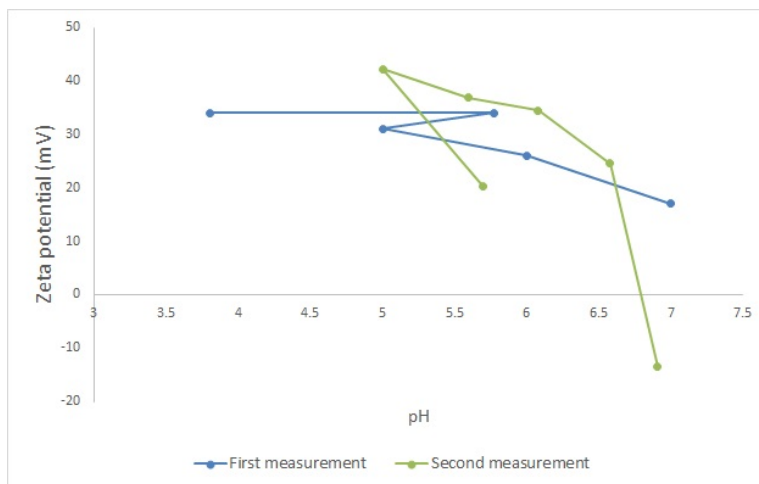


Figure 4.1: The zeta potential as a function of pH. The measurements started at pH 7 and follows the line in chronological order. The hop from pH 5 to a higher pH is not intentional but due to faulty equipment/software.

The sample that was sonified did not show any sign of stability, as it is a clear liquid. This is shown in Fig. 4.2.

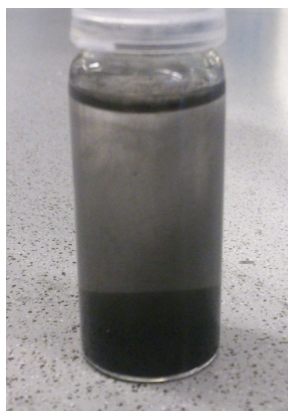


Figure 4.2: The dispersion of LSC in nitric acid after less than an hour after preparation.

4.1.2 PVP as stabilizer

The first sample with PVP as a stabilizer had a high concentration of LSC, which caused the ink to be so thick that it could not flow out of the grad. cylinder on its own as seen in Fig. 4.3. For the sample with a lower concentration it is seen in Fig. 4.4 that PVP is not stable over long periods of time. The content from the milling was mainly sludge and the PSD analysis in Fig. 4.5 shows that the milling does not help to break up agglomerates.

When the solution was subjected to ultrasonic treatment, it was not stable for a day.

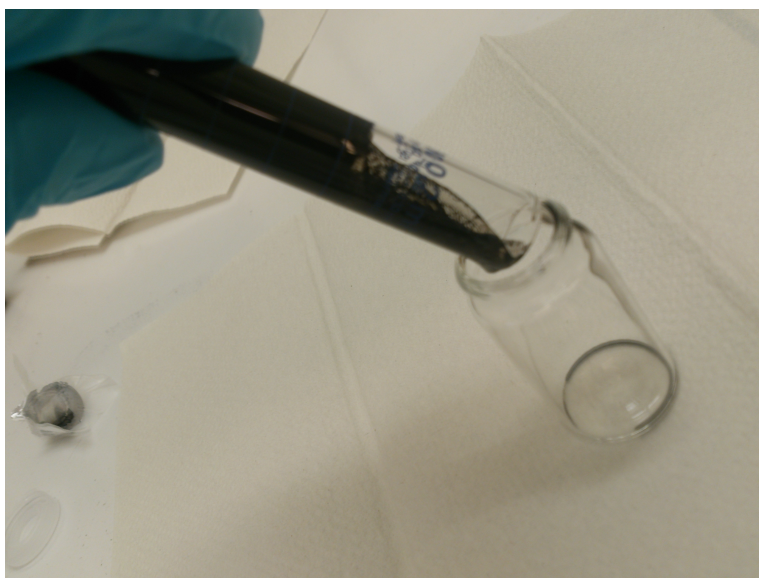


Figure 4.3: High concentration of LSC milled with PVP. The sample was too viscous to flow freely out of the grad. cylinder.

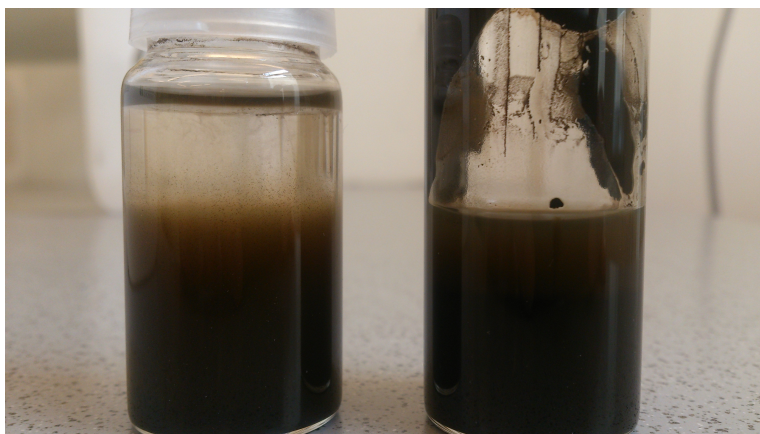


Figure 4.4: Both vials hold content from the milling of PVP, the right vial contains around 50% sludge from the particles.

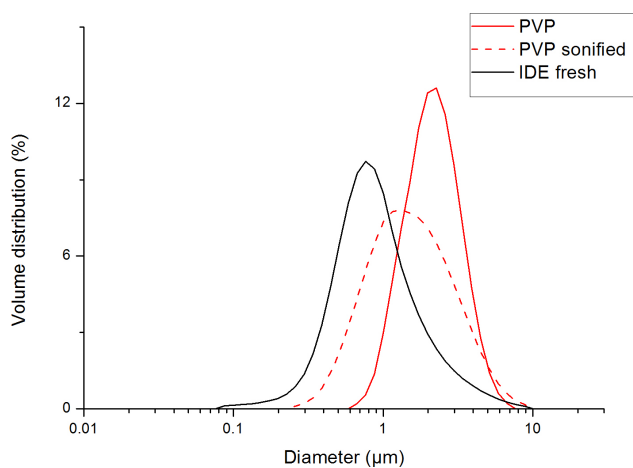


Figure 4.5: The particles that had been ball milled in the second PVP batch were heavily agglomerated, and did not deagglomerate in the milling process. "IDE fresh" is a deagglomerated reference sample.

4.1.3 Dolacol as stabilizer

The results showed that Dolacol was ineffective in use as a stabilizer on its own. The powder was stable for less than a day in isopropanol. In ethanol there were particles on the sides of the glass making it appear like it was stable. This was not discovered until day two and it was thus poured over into a new vial, as seen in Fig. 4.6.

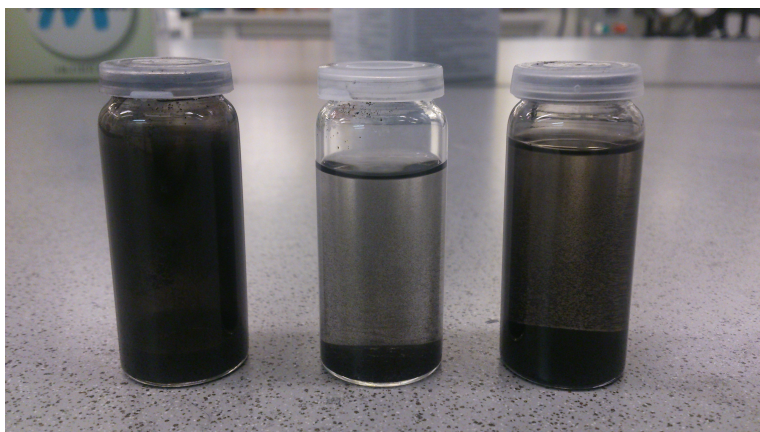
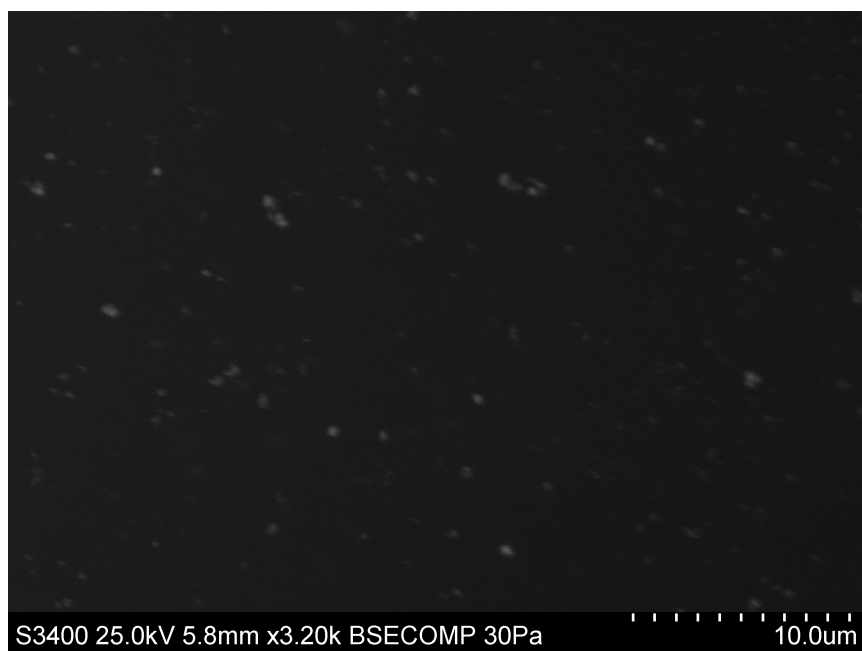


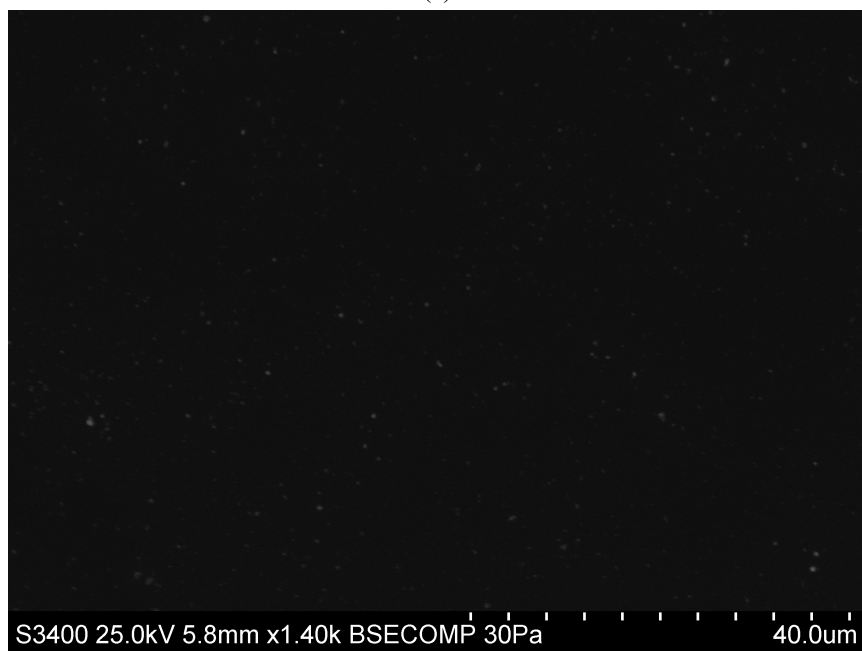
Figure 4.6: From left to right: Original container for ethanol with Dolacol, ethanol with Dolacol after pouring from the original container, isopropanol with Dolacol in original container.

4.1.4 Electron microscopy imaging of wet ink

Only the smaller particles are shown in the wet SEM image in Fig. 4.7 due to their higher stability, and because the electron beam can not penetrate deep enough into the sample to image the larger particles that settle quickly. The imaged particles are suspended in the solution, but some might be stuck to the polymer membrane of the sample holder. Long exposure times would usually not capture the particles because of movements, as shown in Fig. 4.8 and this also leads to agglomeration as seen in Fig. 4.9. These movements are due to the electron beam, as the particles in the isopropanol solution are charged by it.



(a)



(b)

Figure 4.7: LSC particles in isopropanol with ethyl cellulose as steric stabilization.

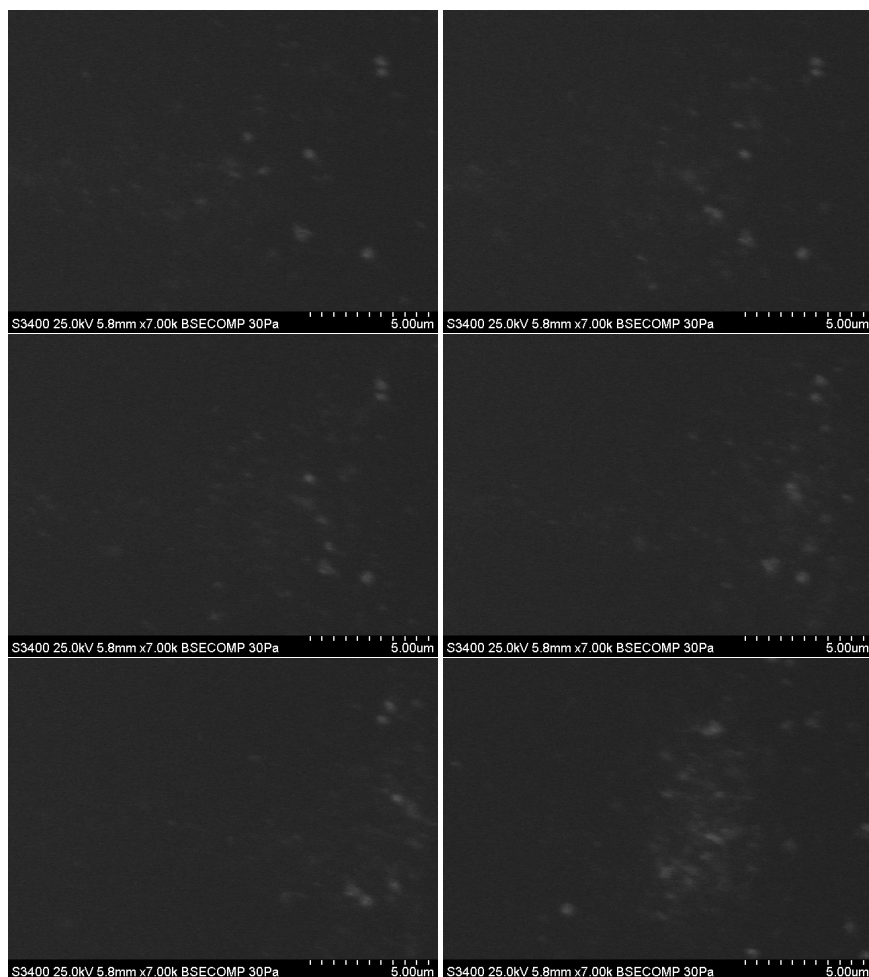


Figure 4.8: LSC particles in isopropanol with ethyl cellulose as steric stabilization. The pictures were taken at the same spot in rapid succession. The order is left to right, top to bottom. Last picture taken slightly to the right of the others.

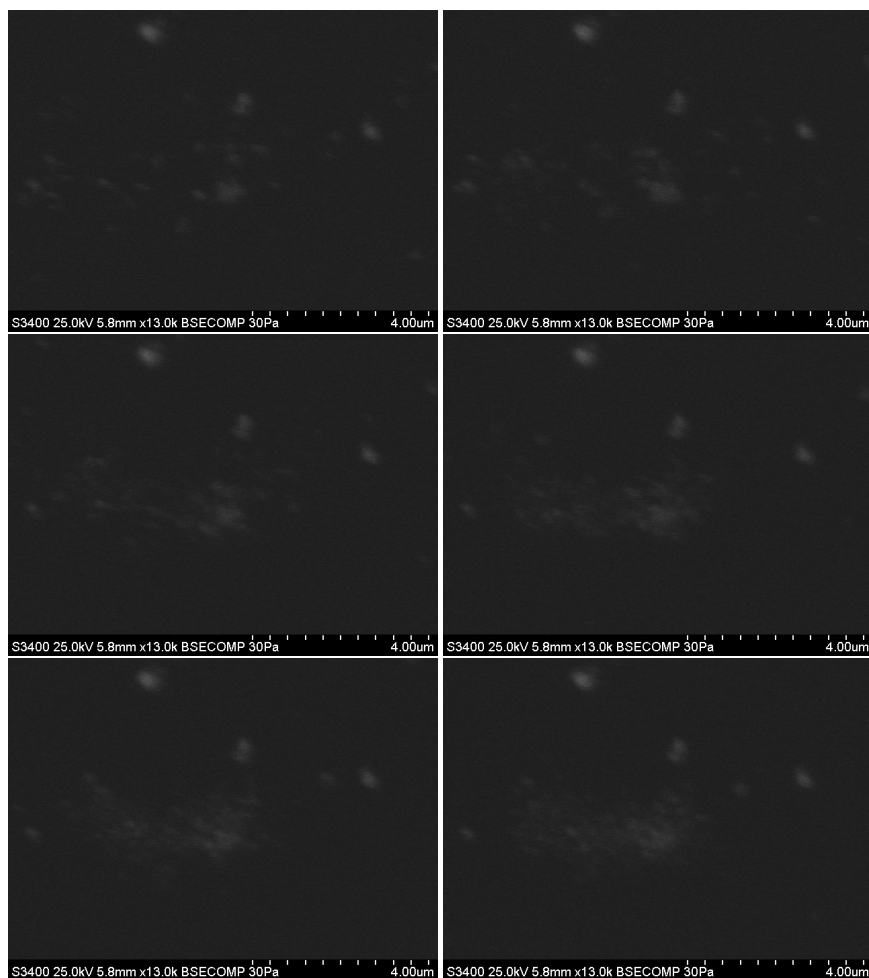


Figure 4.9: LSC particles in isopropanol with ethyl cellulose as steric stabilization. The pictures were taken at the same spot in rapid succession. The order is left to right, top to bottom.

4.2 Size control

4.2.1 Filtration

The filtration of ink is shown in Fig. 4.10 to be effective at removing the largest particles.

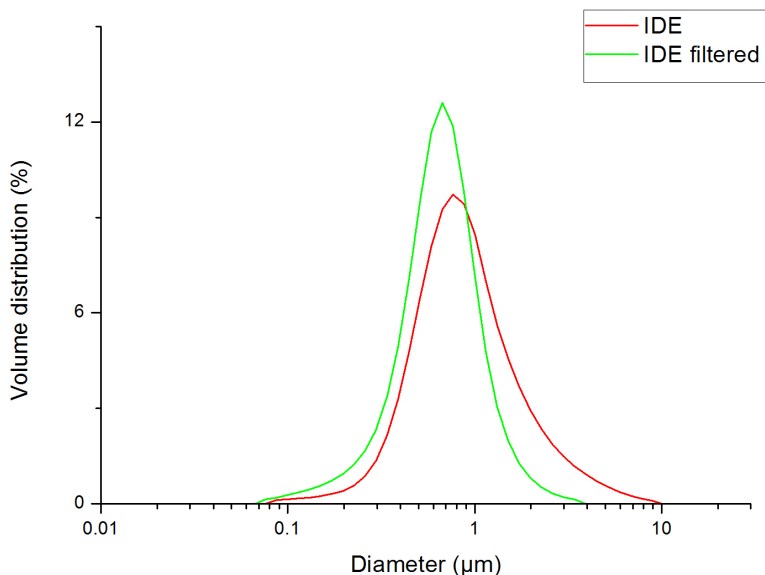


Figure 4.10: Size distribution differences between unfiltered and filtered inks.

4.2.2 Settling

Tests with IE and IDE shows that the largest particles are unstable over time, as seen in Fig. 4.11. Fig. 4.12 shows the average and the sizes below at which 50% and 90% of the particles by volume are situated. In Fig. 4.13 it is seen that the mid and bottom layer have a much larger size distribution, with negligible difference in the maximum size. If one assume that the smallest particles are stable in the solutions, and thus do not settle, one can very roughly estimate how much of the particles are left. While this is not very accurate, it is very practical and simple thing to do. This is done in table 4.1.

4.2.3 Planetary milling

As seen in Fig. 4.14, the particle size can be seen to decrease a bit with the PMIII treatment compared to the others. It is hard to say whether the difference between PMI and PMII is negligible or not. It is also worth to note that during the milling, a large amount of heat was generated, which can cause the isopropanol to evaporate.

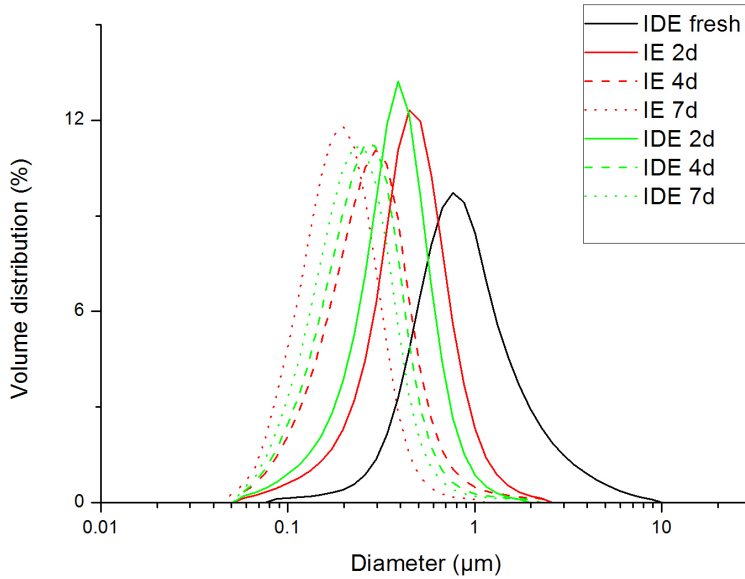


Figure 4.11: Particle size distribution over time in the top 30% layer after settling compared to an unsettled sample.

Table 4.1: Comparison of volume distribution of 100 nm and 150 nm particles in different samples.

| Sample | Vol. % 100 nm | Compared to IDE (Fresh) | Vol. % 150 nm | Compared to IDE (Fresh) |
|--------------|---------------|-------------------------|---------------|-------------------------|
| IDE (fresh) | 0.145 | 1 | 0.242 | 1 |
| IDE filtered | 0.274 | 0.53 | 0.571 | 0.42 |
| IE 2d T3 | 0.605 | 0.24 | 1.279 | 0.19 |
| IE 2d M3 | 0.525 | 0.28 | 1.091 | 0.22 |
| IE 2d B4 | 0.274 | 0.53 | 0.401 | 0.60 |

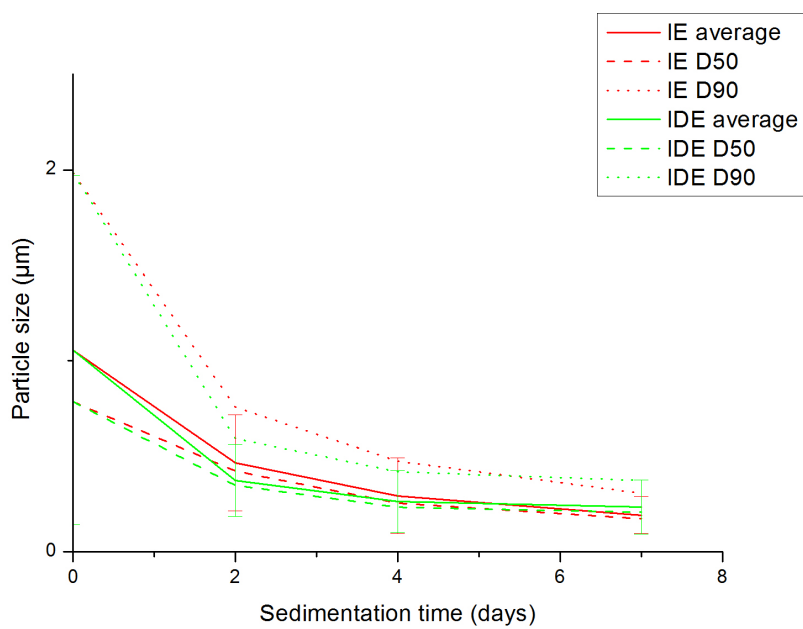


Figure 4.12: Particle size distribution properties over time in the top 30% layer. The standard deviation of the average results are given by the bars. The 0 day sample is in both cases "IDE fresh" from Fig. 4.11.

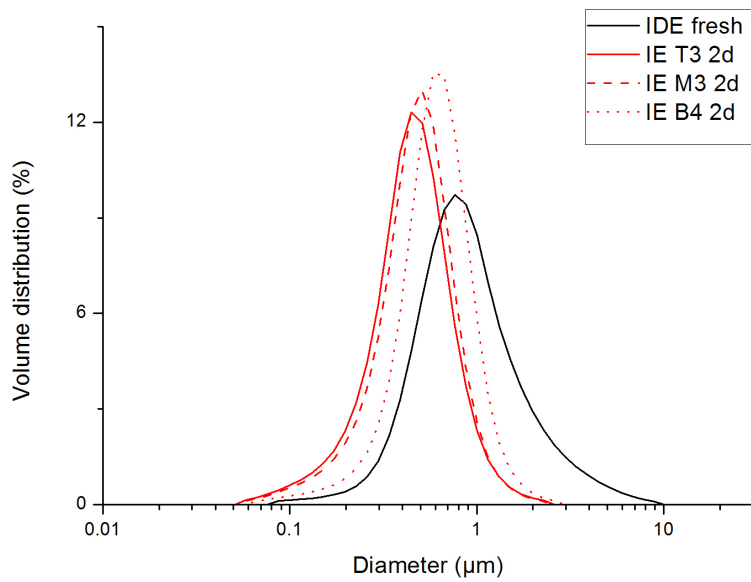


Figure 4.13: Particle size distribution in the top 30% layer, mid 30% layer and approximately bottom 40% layer.

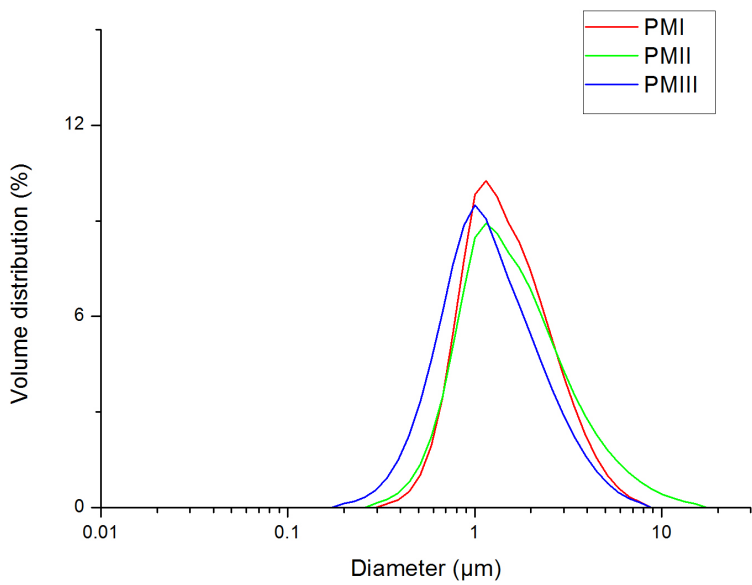
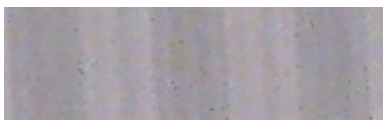


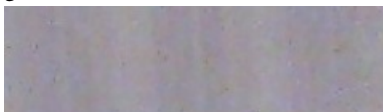
Figure 4.14: Particle size distribution after planetary milling. For explanation of the treatments, see table 3.7.

4.3 Printing

The uneven print in the Fig. 4.15a compared to the print in Fig. 4.15b shows that fresh ink rapidly clogs the nozzles if left idle for a few minutes. The second printing showed that it was possible to print on polyester and that after 17 days, the ink is quite dilute.



(a) Printing without using rinsing programme first



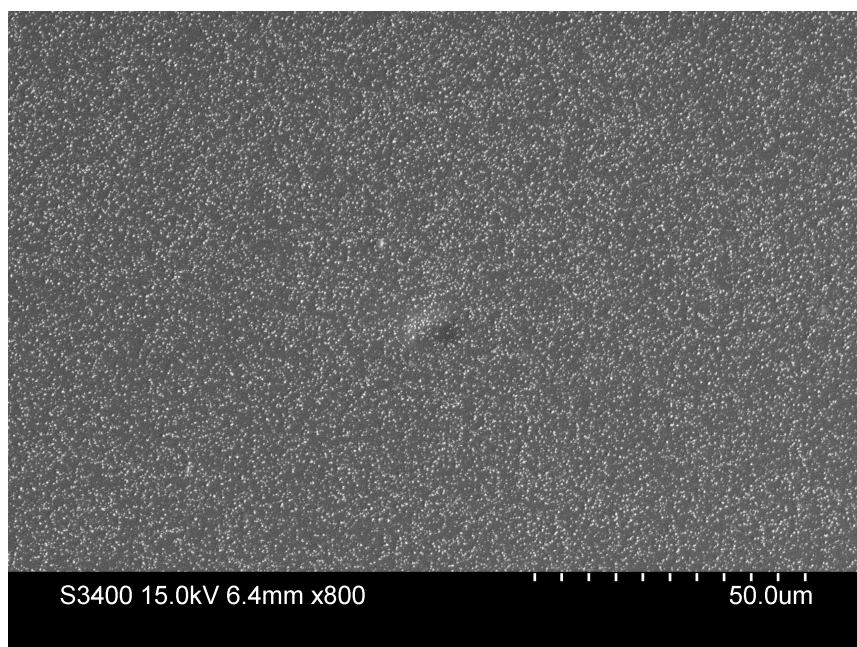
(b) Printing with using rinsing programme first

Figure 4.15: Print of LSC on paper.

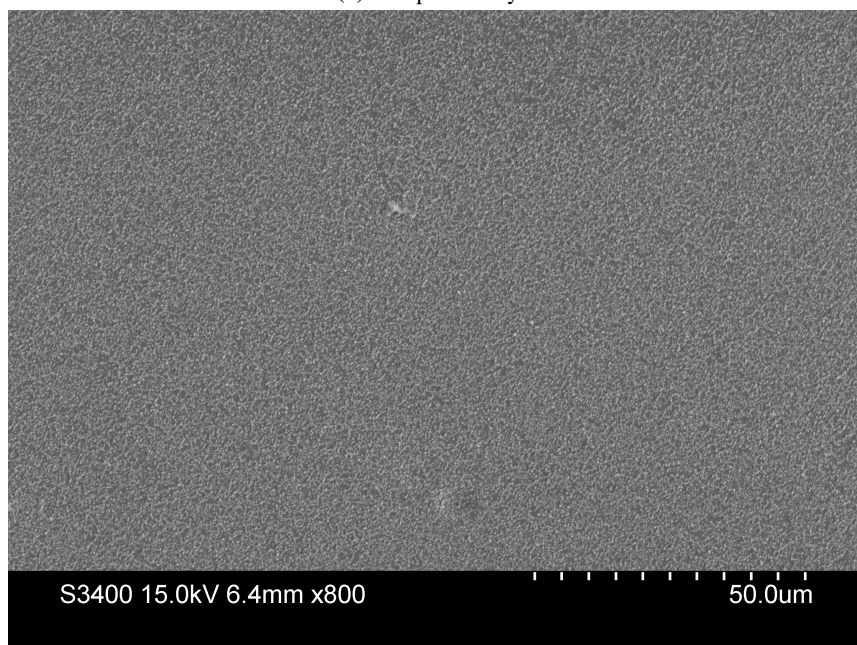
4.3.1 Electron microscopy imaging of printed ink

The prints of LSC on polyester in Figs. 4.16-4.18 shows that even with 4 layers, the print is not thick enough to have a connected layer. From the single layer pictures, one can get a good representation of the particle size and it can be seen that there is a low degree of agglomeration.

In Fig. 4.19 it is shown how it looks when LSC is printed on paper. The paper has a different structure than polyester and it is seen that the ink is not evenly distributed, but forms separate clusters.

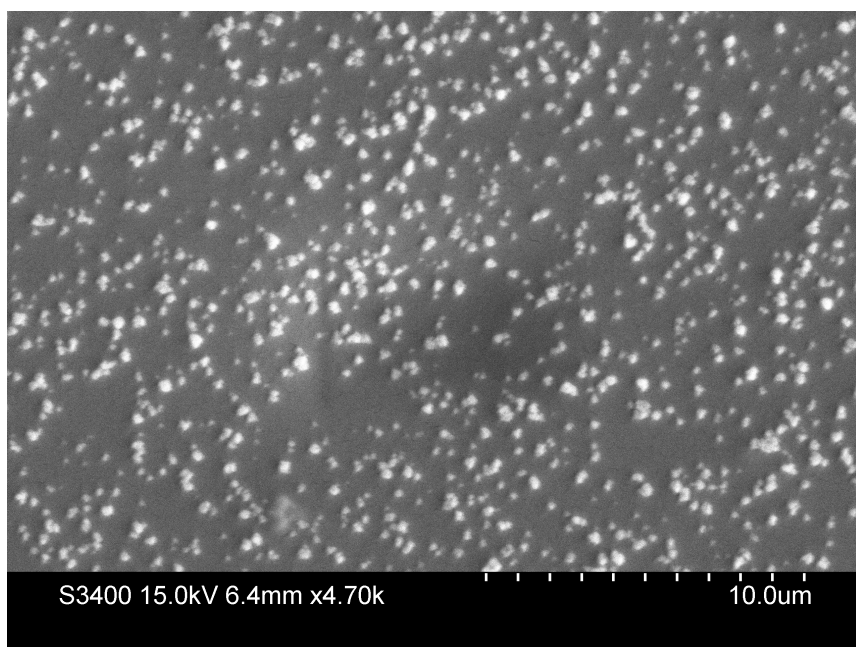


(a) One printed layer

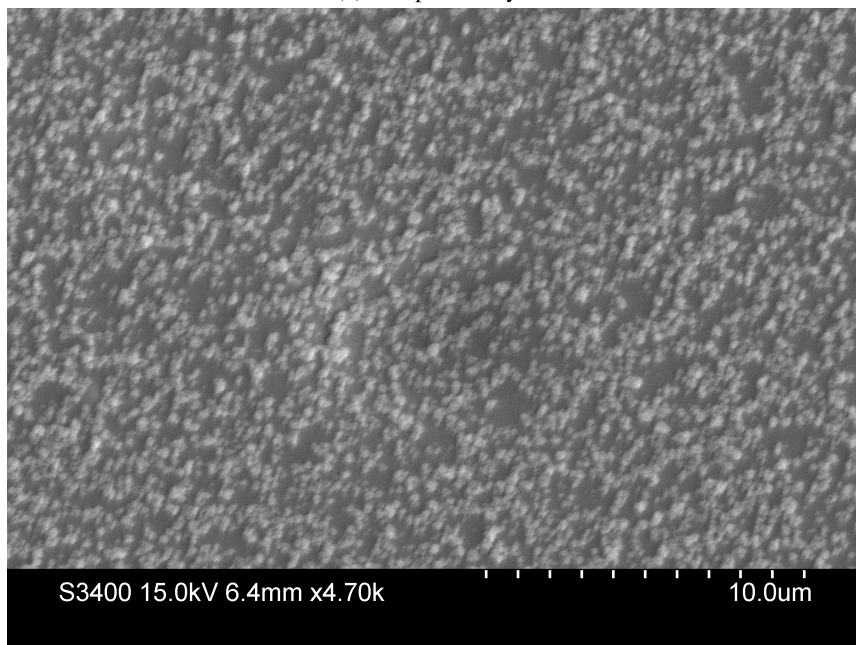


(b) Four printed layers

Figure 4.16: LSC printed on polyester, low magnification

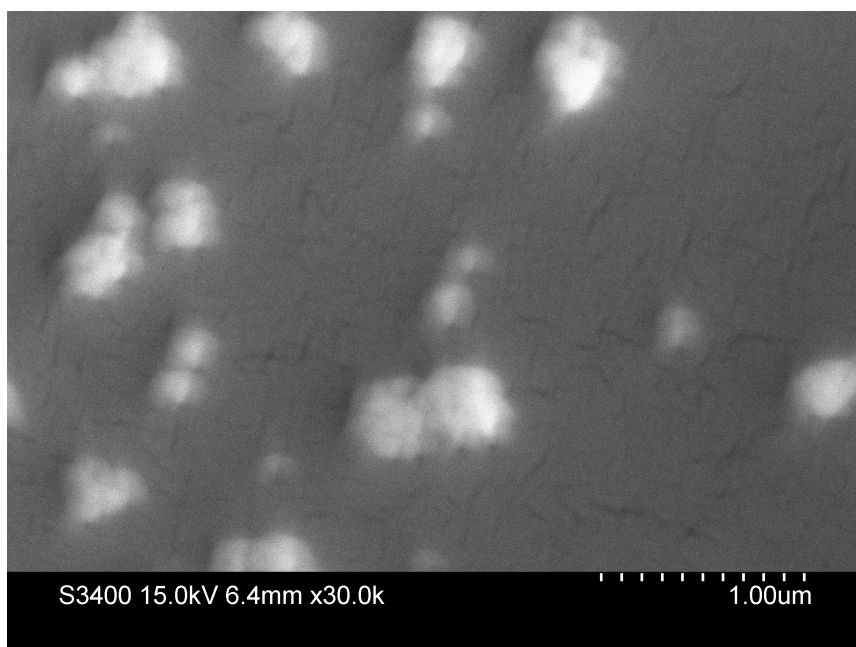


(a) One printed layer

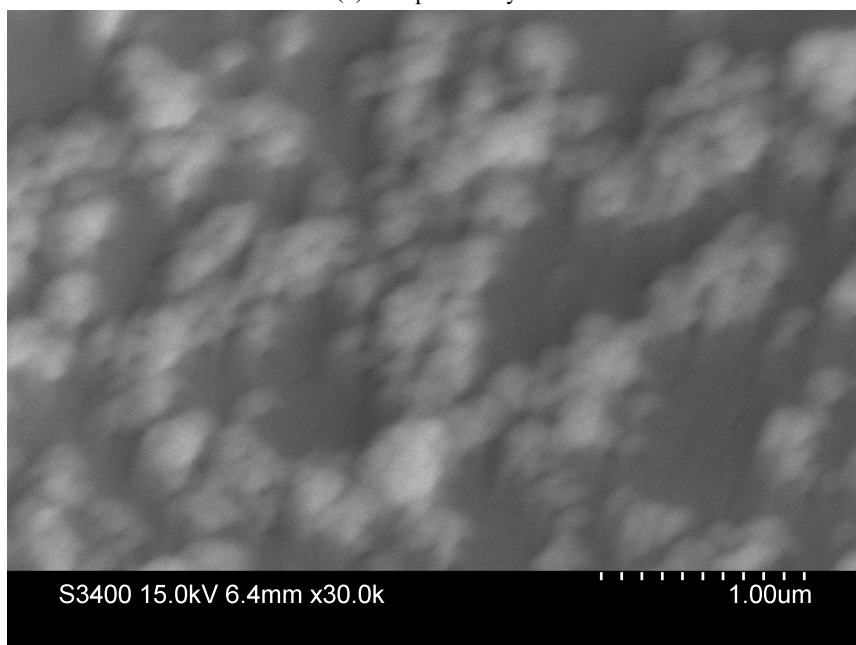


(b) Four printed layers

Figure 4.17: LSC printed on polyester, medium magnification

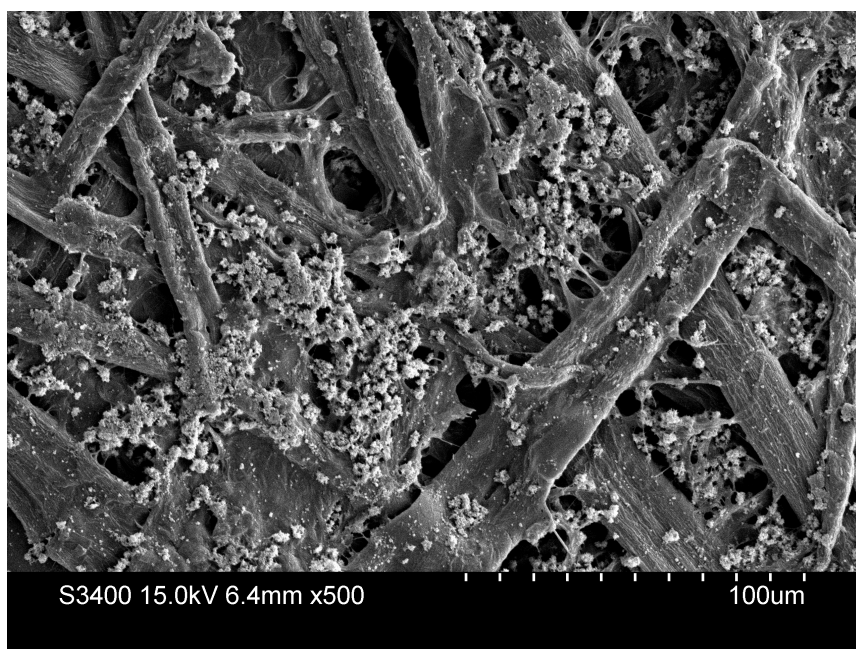


(a) One printed layer

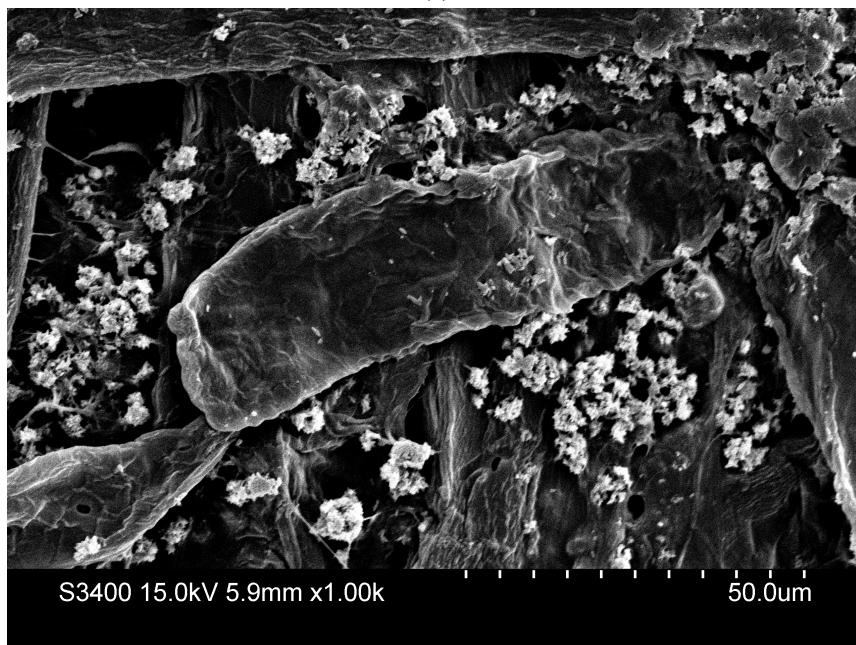


(b) Four printed layers

Figure 4.18: LSC printed on polyester, high magnification



(a)



(b)

Figure 4.19: LSC printed on paper

Discussion

5.1 Stability

From the results, it is clear that all the alternatives tested were worse off than EC, that was proven to stabilize the solutions enough for printing.

5.1.1 Using pH as stabilization

As the equipment to measure zeta potential was unstable, and because it did not work at basic pH values, it is hard say whether the results from the zeta potential measurements are correct. The stability test with nitric acid and LSC did not show any sign of stability.

5.1.2 PVP/Dolacol as stabilizer

The milled PVP solution was partially stable for a short time. The milling resulted in a layer that looked stable, but over time proved unstable. When testing PVP/Dolacol with ultrasonics, the results showed that the particles had no stability. It is believed that this is due to a lack of surface sites where the stabilizing polymers could attach themselves. The milling with PVP is believed to have helped with this, but these new surfaces were not enough for any long term stability like the solutions stabilised with EC has.

5.1.3 Wet ink

As seen in Fig. 4.7, the particles are well dispersed in the solution. The largest particles imaged here are around 1 μm in size. Though, this is as expected, since it is only the top layer that gets imaged, so the larger particles are likely to be too far down to be seen. The "tails" that are seen on the particles could either be due to long exposure time or due to agglomeration. As seen in Fig. 4.8, the particles are heavily affected by the electron beam, which leads to agglomeration as seen in Fig. 4.9.

5.2 Size control

5.2.1 Filtration

The filtration proved effective in removing the largest particles. The filters used in this case were quite expensive compared to the amount it could filtrate, and filtration leads to a large loss of material. The loss in this case is estimated to be around 50% from the results in table 4.1. These two drawbacks would rule out filtration as a main method for controlling the size, but it can be used in conjunction with other techniques as an extra safety barrier at the lab.

5.2.2 Settling

In the project thesis[6], it was assumed that the stability problem was not size related, as the stable top phase had the same PSD as both the bottom phase and the unsettled reference sample. The results of the sedimentation here contradicts that result. This is believed to be due to the sampling. In the project thesis, the top layer was decanted into the sample container. It could either be due to the use of decanting instead of siphoning, or just careless handling of the grad. cylinders causing particles to redisperse.

As seen in Fig. 4.12, IDE and IE do not deviate much from each other and they switch positions in the graph. The measurements were done several times on the same samples and they showed close to identical results. As it was only prepared one sample for each sedimentation trial, it is unknown what the range of deviation is from preparing the samples. So it is unknown whether Dolacol has an effect on the samples. Judging from the previous samples with only Dolacol, there is either no effect or a very small one.

These results shows that sedimentation can be used to remove the largest particles. The maximum size from Fig. 4.11 and D90 size from Fig. 4.12 is both good after two days, though, by comparing the 2 day graph with the "fresh" graph, one can see that large amounts of the particles are gone from the top layer. From the rough assumptions in table 4.1 this leads to a decrease in particle density to around 1/5th of the original after only 2 days.

The bottom layer has a much higher particle density than the mid and top layer of the settled solutions. This could be due to the largest particles settling faster and they are thus at the bottom of the sediment and not in the bottom sample which will probably gain some of the upper sediments due to disturbances and because it was decanted out, which could lead to some sediments to be transferred.

5.2.3 Planetary milling

The planetary milling was unable to reduce the particle size significantly. The milling time might have been too short for this, or the particle density too low. The increase in the number of balls seems to increase the milling efficiency, this thought to be due the increase in surface area where the milling takes places, as the particles are grounded either in between balls, or between the balls and the wall of the pot. More milling time would increase the chance of the particles being broken apart but would also lead to more contamination from the grinding equipment. It could also cause problems due to the heat generated, as the

solvent is isopropanol with a high vapour pressure. An increase in particles would lead to a more effective grinding process due the increase in chance for a particle being broken apart. It might be possible to use planetary milling to reduce the particles to a satisfactory size, but longer grinding time and a higher particle count are recommended.

5.3 Printing

The ink was successfully printed, though there were some problems with the ink clogging the nozzles if left idle for too long (minutes), but this was solved by using the printers rinsing programme.

When printed on paper, the particles seem to form separate clusters, this might be due to the isopropanol getting drawn into the paper, creating a flow that moves the particles.

In the printed layer shown in Fig. 4.17 a low degree of agglomeration and an even distribution of the particles is observed. This is positive, but the layer is not connected because the particle density of the ink is too low. Even with 4 printed layers, it is not enough to create a dense film. This is partially because the ink was settled for 4 days to remove the largest particles, leading to severe thinning of the ink. The removal of the largest particles by the most convenient methods (filtering and settling) leads to a large reduction in the powder content which is a problem. A higher powder content is needed irrespectively of how much is lost during size control.

A large nozzle size is recommended, as a nozzle size around $50\text{ }\mu\text{m}$ would increase the resistance to clogging, although it would decrease the printing resolution. For a thick cathode layer, there is less need for axial resolution as it needs more thickness than electrolyte layer, but the lateral resolution of the print would be also be compromised by this. Whether this is a problem depends of course on the need for lateral resolution in the design of channels in the SOFC stack.

Even with a larger nozzle, the solutions are still unstable, and printing would have to be done swiftly after homogenization of the ink. And even then, the largest particles ($>2\text{ }\mu\text{m}$) would have to be removed to avoid nozzle blockage.

Unfortunately there have been no tests on a relevant substrate, like an electrolyte layer or a cathode/anode interlayer. This should be done to see whether the ink has the right droplet properties.

Conclusion

It seems from the settling experiments that ethyl cellulose is quite effective to avoid agglomeration, and that it is mainly the particle size that causes settling. The particles are well dispersed in the solution but tends to settle. To reduce settling it might be possible to use a different solvent where the particles have more resistance to settling. Alpha-terpineol could be used for this, but it has a high viscosity and this might be too high to print with at ambient temperatures.

The isopropanol and ethyl cellulose mixture is mainly hampered by the large size distribution of the spray pyrolyzed powder. If the largest particles ($>2\text{ }\mu\text{m}$) are removed, it is possible to redisperse the particles shortly before printing and use a semi-stable ink. While it is not optimal, this could be an acceptable drawback for the production of fuel cells and could possibly be automated by having an ultrasonic system to deagglomerate particles and homogenize the ink shortly before printing.

The printing showed that the particles are evenly distributed and that it is possible to use the isopropanol ink for piezoelectric printers. A larger nozzle size should be considered, especially if the particle size is large. The powder load of the ink should be increased as it has problems covering the substrate properly.

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Appendix

This is contained in the following pages:

- Conditions for zeta potential measurements.

Zeta SOP

SOP Name : Espen (pH)

| Measurement Parameters | Condition Name | :auto save |
|------------------------|----------------|------------|
| | User Name | :Common |

File Name :
Group : IMT
File Save : Auto
Manual Temp. Setting : Yes
Temperature : 25
Equilibrating : Yes
Statistical Summary : No
Statistics File Name :
Repetition : 3
Auto Print : Manual
Intensity Adjust : Yes
Equilibration : 0
Wait Time : 0
Pinhole : 50

Sample Information :

| Analysis Parameters | Condition Name | :Smoluchows |
|---------------------|----------------|-------------|
| | User Name | :Common |

Lorentzian Fit : 1 peak
Conversion Equation : Smoluchowski
ACF : Yes
3D Plot : Yes
Distribution Graph : Zeta Potential
Peak Values : No

Comment :

Zeta SOP

SOP Name : Espen (pH)

| Cell Parameters | Condition Name | :Flow Cell (ES pH 2) |
|-----------------|----------------|----------------------|
| | User Name | :Common |

Measurement Item : Zeta Potential
Measurement Type : Type4
Cell Name : Flow Cell
Cell Type : Flow Cell
Cell Constant : 70
Cell Center (X) : 7.26
Cell Center (Z) : 6.345
Correlator Type : Linear
Accumulation Times : 10
Applied Voltage : Fixed
Select Voltage : 60
Polarity : Auto
Cell Position : 1.00/0.00/-1.00

(Test)
Polarity :NEGATIVE

Comment :

(Titration)

Titration Mode : pH Titration
pH Table : 7.00/6.50/6.00/5.50/5.00/4.50/4.00
pH Tolerance : 0.1
Additive Volume Table : 10
Circulation Time : 1
Circulation Time Table :

| Diluent Properties | Condition Name | :water |
|--------------------|----------------|---------|
| | User Name | :Common |

Diluent Name : WATER
Refractive Index : 1.33
Viscosity : 0.89
Dielectric Const : 78.3
Comment :