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Optimisation of CGO suspensions for inkjet-printed SOFC electrolytes

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Abstract

A detailed procedure for the preparation of gadolinium doped (10 mol%) cerium (IV) oxide (CGO) suspension for inkjet printing is described in this paper. The optimisation of inkjet printing parameters for the deposition of solid oxide fuel cell electrolytes was also performed using a custom-built drop visualisation system. Additionally, the uniformity of the deposited drop relics on porous substrates was evaluated. The ink used in this study was an evaporative type comprising a solvent mixture of terpineol and methanol, ethyl cellulose and CGO powder. Successful printing of regular drops was achieved after printing optimisation. It has been demonstrated that inkjet printing is a promising technique for high quality membrane fabrication for applications including solid oxide fuel cells. The ink formulation and optimisation procedure would also be applicable for other ceramic ink development.

Keywords: Inkjet printing; Suspension; SOFC; Electrolyte; Optimisation

1. Introduction

There is an increasing trend of utilising inkjet printing technology for the production of various electro-ceramic devices such as solid oxide fuel cells (SOFC)[1,2] and superconductors.[3] Inkjet printing has proved to be a versatile and robust manufacturing technique for creating continuous coatings[2] and more complex two- and three-dimensional structures,[3,4] offering the capability to produce films of accurately controllable thickness and high-resolution patterns. It is also cost effective, requiring only modest investment and minimising wastage of expensive precursor materials.

SOFC is an area of application of inkjet printing, currently receiving particular attention. Producing a thin and dense electrolyte membrane is a very important requirement for a practical SOFC operated at intermediate temperatures, as described by Steele et al.[5] However, most conventional non-vacuum techniques such as screen printing and dip coating cannot achieve dense coatings thinner than 10 μm.[6,7] Recently Tomov et al. have shown that it is possible to produce a gas-tight YSZ electrolyte of 5 μm reproducibly by inkjet printing, which sets a new benchmark for an SOFC electrolyte using cost effective methods.[2]

In order to create an electro-ceramic device using inkjet printing, the first step is to create a stable ink. Ceramic particles with a controlled size distribution can be made into an ink by dispersing them in a fluid system. The ink is then deposited by drop-on-demand (DOD) inkjet printing, producing a green ceramic structure, which is subsequently sintered to obtain the final ceramic. The evaporation type has been widely used in application such as paint, and conductive ink.[8] The ink is solidified via solvent evaporation, where a volatile solvent is used as the fluid system in which ceramic particles are dispersed. After drops are deposited onto the substrate, evaporation of the solvent takes place, which will leave the solid particles behind. This type of suspension can produce a high packing density of solid particles[7]; hence it is suitable for making dense structures and films. In this study, the ink will be based on the solvent evaporation type of suspension, since making a dense SOFC electrolyte is the primary objective. An evaporative ink system usually consists of three main components: ceramic solid particles, polymeric dispersant and solvent. The solid particle provides the raw material to produce the ceramic. The polymeric dispersant not only serves to stabilise the particles (via steric stabilisation),[16] but also acts as a binder and relieves drying stresses (preventing cracking).[9]

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Polymeric dispersant can also be used to tailor the rheology of the ink. In some cases polymeric dispersant are used as a fugitive agent to create porous structures.[10] Finally, the solvent disperses polymer-coated particles and carries them within a fluid system.

In order to successfully produce ceramic films by inkjet printing, the ink must satisfy a numbers of requirements. First, the suspension must be stable (i.e. no sedimentation or excessive agglomeration). Secondly, its rheological properties must be such that they can generate regular drops consistently in the chosen inkjet printing system. This criterion has been expressed in the literature as a constraint on the reciprocal of the Ohnesorge number ($Z = Oh^{-1}$, $1 < Z < 10$):

$$Oh = \frac{\eta}{(\gamma \rho a^{0.5})}$$

where ρ, η and γ are the density, dynamic viscosity and surface tension of the fluid respectively, and a is a characteristic length(after Derby).[11] Next, the deposition of the solid must be uniform. One potential problem during the solidification of a drop of an evaporative type ink is known as the "coffee staining" effect. The effect has been studied and well documented on both dense[12] and porous substrates.[13] The coffee staining effect, explored first by Deegan et al.,[12] represents the formation of a deposit with non-uniform thickness on drying, with more particles deposited near the perimeter. Deegan et al. pointed out that this effect was caused by contact line pinning of a drying drop, followed by evaporation of solvent along the perimeter of the drop where the exposure area is greatest. As a result a driving force is created causing suspension to flow outwards from the centre of the drops in order to compensate for the loss of solvent, creating a thick rim around the perimeter of the drops. Therefore it is important to minimise the coffee staining effect in order to produce well-defined and controllable structures or smooth coatings.

Ideally for the deposition of multiple coatings, the solvent should have a fast evaporation rate. However it has been reported that using a highly volatile solvent would enhance the coffee staining effect since there is a greater driving force.[13,14] One way to minimise the coffee staining effect is to use a solvent mixture incorporating a low vapour pressure solvent with low surface tension.[15] In this way an opposing flow to the evaporation flow, known as Marangoni flow, can be generated. Dou et al.[13] has exploited this technique and obtained uniform drop and line deposition on a dense substrate; but the coffee staining effect was still observed on both drops and lines when they were deposited on a pre-dried printed layer which represented a porous substrate.

In this study, we explored a number of combinations of solvent systems in order to minimise the coffee staining effect on a porous substrate, while maintaining ink stability and good jetting performance. A systematic approach was taken: first a number of stable suspensions were made, next the printing/jetting parameters were optimised for each ink, and finally the ink was deposited on a porous substrate to study the droplet surface uniformity.

2. Experimental

2.1. Ink preparation

10 mol% gadolinium doped cerium (IV) oxide (99.99% purity, Sigma–Aldrich) powder was wet milled (powder dispersed in isopropanol, 3YSZ milling balls) in a planetary mill for 8 h to ensure a uniform particle size of around 400 nm (measured by Zetasizer 3000HS, Malvern Instruments). Ethyl cellulose (99.9%, Sigma–Aldrich) was used as the polymeric dispersant for ink stabilisation. Methanol (reagent grade, Sigma–Aldrich) was chosen to be one of the fluid systems because it can readily dissolve the polymeric dispersant and its high volatility allows fast drying of the drops. Terpineol (Sigma–Aldrich) was selected as the low vapour pressure solvent, inducing the Marangoni effect. It also played the role of a natural dispersant of the oxide particles and has excellent miscibility with the polymeric dispersant and methanol solvent.

The minimum amount of polymeric dispersant required for stabilising the ink was determined prior to ink preparation. Since the focus of this research was on creating a dense film by inkjet printing, the polymeric dispersant content was kept to a minimum to ensure high density during subsequent sintering, as excess polymeric dispersant content could also introduce porosity. To determine the minimum amount of polymeric dispersant required, several concentrations of polymeric dispersant were prepared by mixing 0.005–0.1 g of polymeric dispersant with 0.5 g of 10 mol% gadolinium doped cerium oxide and 5 ml of methanol in polyethylene bottles by a traditional ball milling technique using 3YSZ milling media for 72 h. The obtained inks were subsequently centrifuged at 1000 rpm, and then visually inspected for signs of sedimentation, to assess their stability. The minimum amount of polymeric dispersant was found to be ~10 wt% of the ceramic powder.

Different terpineol and methanol mixtures were prepared to produce inks with different rheological parameters, and to investigate both the Marangoni effect and the coffee staining effect. Six inks with terpineol/methanol ratios from 70:30 vol% to 20:80 vol% were created, all inks containing a constant polymeric dispersant content (10 wt% relative to the ceramic powder) and a constant particle mass load (5 wt%, equivalent to 0.7 vol%). Each component was carefully weighed and the ink prepared as described above.

2.2. Inkjet printer

The printer used for this experiment consists of an electromagnetic single nozzle printhead with a 90 μm ruby orifice, modified from a Domino MacroJet printer, mounted 10 mm above the substrate on a Roland pen plotter. The printhead is based on the operation of an electromagnetic solenoid valve. Ink is delivered under pressure to a reservoir which is sealed by a rubber-tipped piston. A pulse of current passed through the solenoid generates a magnetic field, driving the piston up. The duration of that pulse, termed the "opening time", controls the duration for which the orifice is left unsealed and a controlled

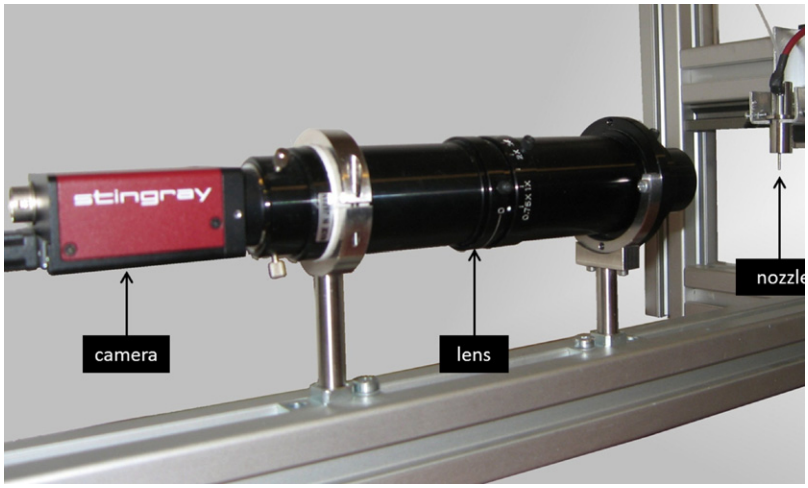

Fig. 1. Annotated photograph of the drop visualisation system.

volume of the suspension is ejected from the nozzle, forming a droplet. In this particular design, the external solenoid is remote from the orifice and print chamber, separating the ink from the heat generated by the solenoid; hence parameters such as viscosity can be kept constant.

2.3. Characterisation

A custom-built drop visualisation system was used to track the drop generation process and determine the optimum range of printing parameters for the ink (Fig. 1).

Drops are imaged over a distance up to 4.6 mm below the nozzle during ejection using a camera (Stingray, Allied Vision Technologies) with a telecentric zoom lens. The drops are back-lit using strobed LED illumination, employing custom-designed electronics to trigger both the strobe and the camera shutter at a selectable delay after drop ejection. For the visualisation studies here, inks were jetted at 10 Hz, with the strobe delay time starting from 500 μs after the start of the current pulse delivered to the print-head. A ceramic ink with a 50:50 volume ratio of terpineol and methanol (Inktm55, see Table 1) was selected for the drop visualisation study. This ink composition was selected because it was stable and could be jetted with a pressure sufficiently below the permitted maximum working pressure of 1000 mbar to allow a good range of adjustment. The optimisation of the deposition was based on the variation of two printing parameters, the opening time and the ink pressure, which together control the drop volume and velocity. A total of 25 printing parameter combinations were investigated, with the pressure ranging from 400 mbar to 800 mbar in 100 mbar intervals and the opening time varying from 400 μs to 600 μs in 50 μs intervals. The obtained images were then thresholded into binary images for analysis using an automated algorithm. The same equipment was also used to observe the time taken for liquid infiltration into the porous substrate and for the evaporation of the solvent. Dark field optical microscopy was used to confirm the macroscopic quality of the drop relics. Finally, a rotational viscometer (Brookfield DV-E) was used to obtain rheological information, measurement was conducted with shear rate of 5.8 s^{-1} at room temperature.

2.4. Film fabrication

A complete coating of CGO was deposited on a porous tape cast NiO/YSZ cermet substrate (500 μm thick, 25% porosity) which was pre-sintered at 1100 °C (CEREL, Institute of Power Engineering, Poland) prior to printing. The printing of CGO was carried out with the jetting parameters optimised in the drop visualisation study, a jetting frequency of 40 Hz and a plotter movement speed of 2 cm/s. A square array of droplets with a spacing of 0.5 mm was used in such a manner to provide complete coverage. A total of ten layers were deposited and the printed layers were subsequently sintered at 1400 °C for 4 h in order to obtain a dense film. The surface of the fabricated film was examined by SEM.

Table 1
Summary of ink (0.7 vol%) properties for different terpineol/methanol volume ratios.

Ink	Volume ratio (terpineol:methanol)	Minimum ink pressure for jetting (mbar)	Viscosity (cP)	Sedimentation after 2 h
Inktm73	70:30	Not printable	25.6	No sedimentation
Inktm64	60:40	700	23.1	Negligible sedimentation
Inktm55	50:50	400	19.2	Negligible sedimentation
Inktm46	40:60	200	15.2	Negligible sedimentation
Inktm37	30:70	100	12.5	Approximately 5 vol%
Inktm28	20:80	100	7.2	Approximately 5 vol%

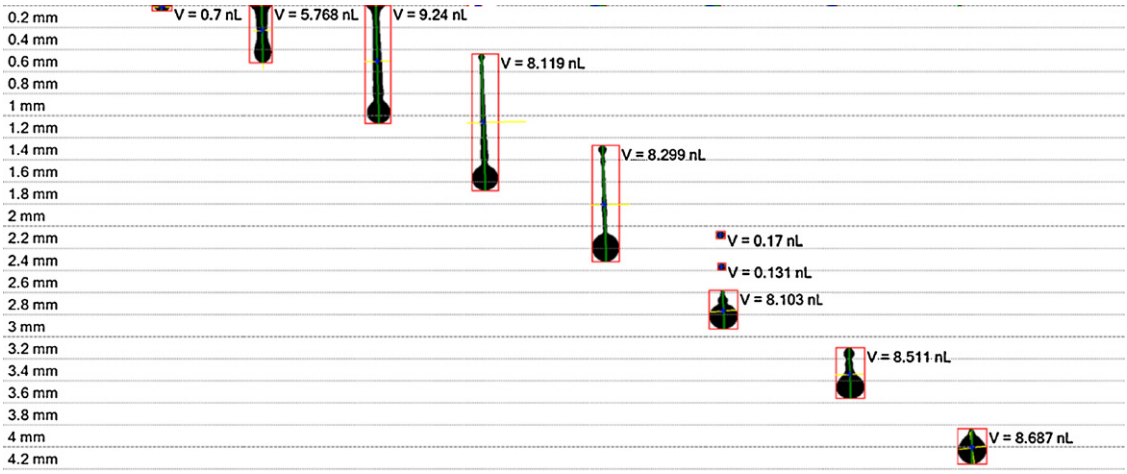

Fig. 2. Montage of images from the drop visualisation system showing the jetting of ink 50:50 volume ratio of terpineol and methanol (inktm55) under a pressure of 400 mbar and with a 450 μs opening time. The first frame was taken 650 μs after the printing device was triggered and the time interval between each frame is 300 μs.

3. Result and discussion

3.1. Ink stability

All inks were left to rest for 2 h before testing their stability by visually inspecting the amount of sedimentation. All inks exhibit adequate stability after 2 h, but the degree of sedimentation increases as the terpineol content decreases. The highest tested terpineol content (inktm73) yields the most stable ink (no observed sedimentation). We believe this effect to be related to the theta condition of solvent and polymer interaction. It is presumed that the polymer forms an ideal chain configuration when dispersed in terpineol, resulting in expanded volume, so those chains clinging to the particle create the maximum repulsion between each other. Hence they are stable for a longer period of time.[16]

The ink properties are summarised in Table 1. As expected, the viscosity increased with increasing content of terpineol (36.5cP), which has a much higher viscosity than methanol (0.5cP). In an inkjet printing device, drop ejection is hindered by a high viscosity solvent,[17] since it requires more energy (pressure) to generate a drop. Jetting could not be achieved for mixture inktm73 even at the highest tested pressure of 1500 mbar. For inktm64 the jetting only initiated above 700 mbar which is too high for practical printing. The optimum range for the terpineol and methanol volume ratio was therefore found to be between

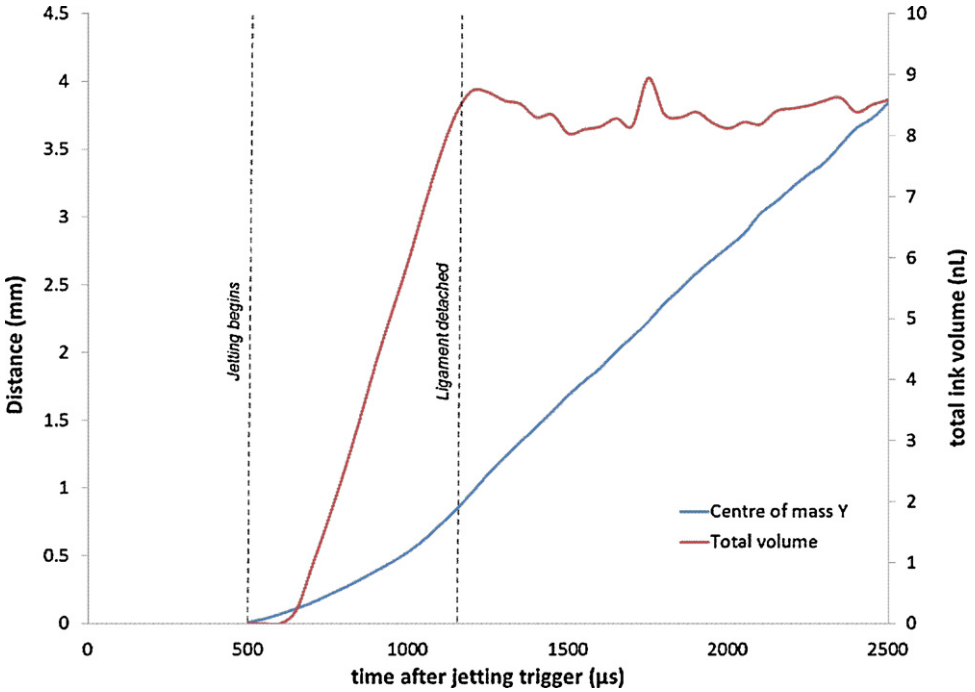

Fig. 3. The position of the centre of mass and the total ink volume as a function of time after the jetting trigger, as obtained from image analysis of drop visualisation images, for ink inktm55 jetting with a pressure of 400 mbar and a 450 μs opening time.

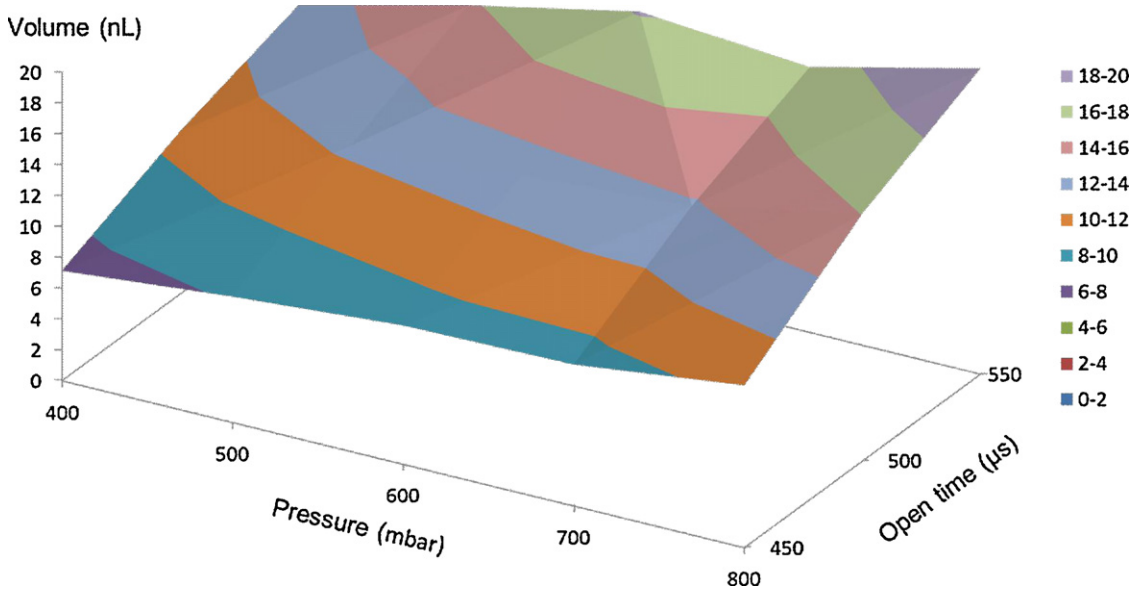

Fig. 4. Surface plot of drop volume against pressure and opening time.

50:50 and 60:40 in order to satisfy both jetting and ink stability criteria.

3.2. Jettability

Although inktm64 could also be jetted at below our maximum working pressure (1000 mbar), as described in Table 1, this leaves little range for pressure adjustment so the threshold for printability was set at inktm55. Printing parameters were determined and optimised for this particular ink. Drop visualisation was used to study the drop generation process for each combination of pressure and opening time and, in conjunction with image analysis, to determine the corresponding drop velocity and drop volume. The greatest advantage of the drop visualisation system is that it allows rapid examination of whether the rheological condition of the ink is suitable for printing. Ideally, any ink should be tailored in such a way that each triggering event results in a single drop, without satellite drops, before reaching the substrate. Using a pressure of 400 mbar and an opening time of 450 μs to illustrate the drop formation behaviour, which is shown in Fig. 2, the initial drop breaks into a series of small drops (up to 4) after it detached from nozzle, but the smaller drops then soon catch up with the main drop and form back to a single drop. Hence this ink can be used ensuring the condition of no satellite drop formation.

From further quantitative analysis, the drop visualisation system also allows other information such as the velocity and drop volume to be obtained. Fig. 3 shows the estimated centre of mass position and volume of the drops as a function of time. The first ink ejection is observed 650 μs after the electrical pulse is

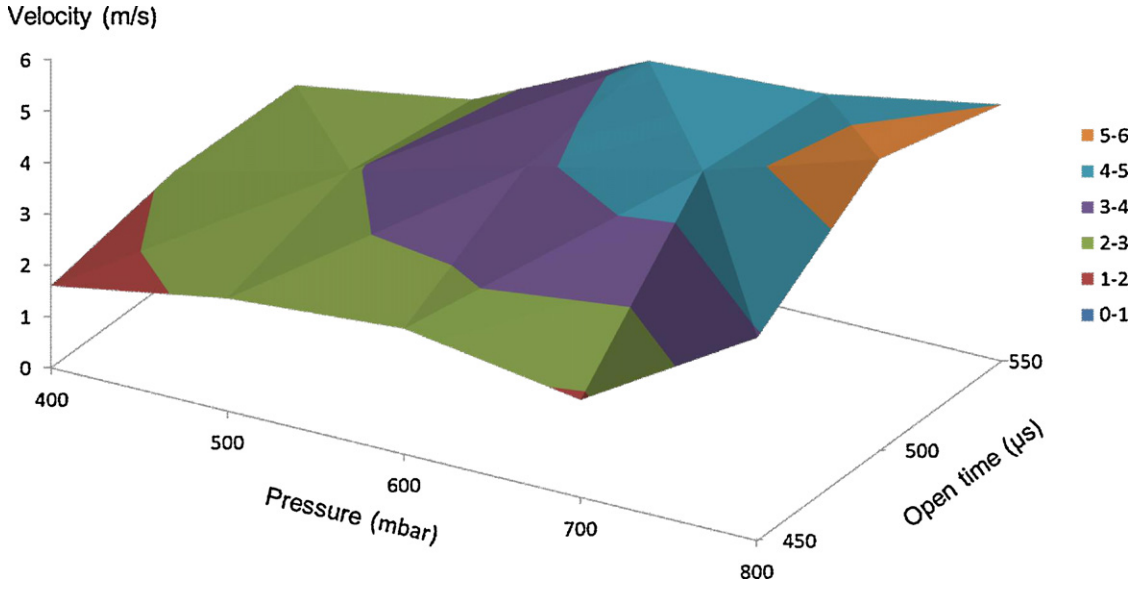

Fig. 5. Surface plot of drop velocity against pressure and opening time.

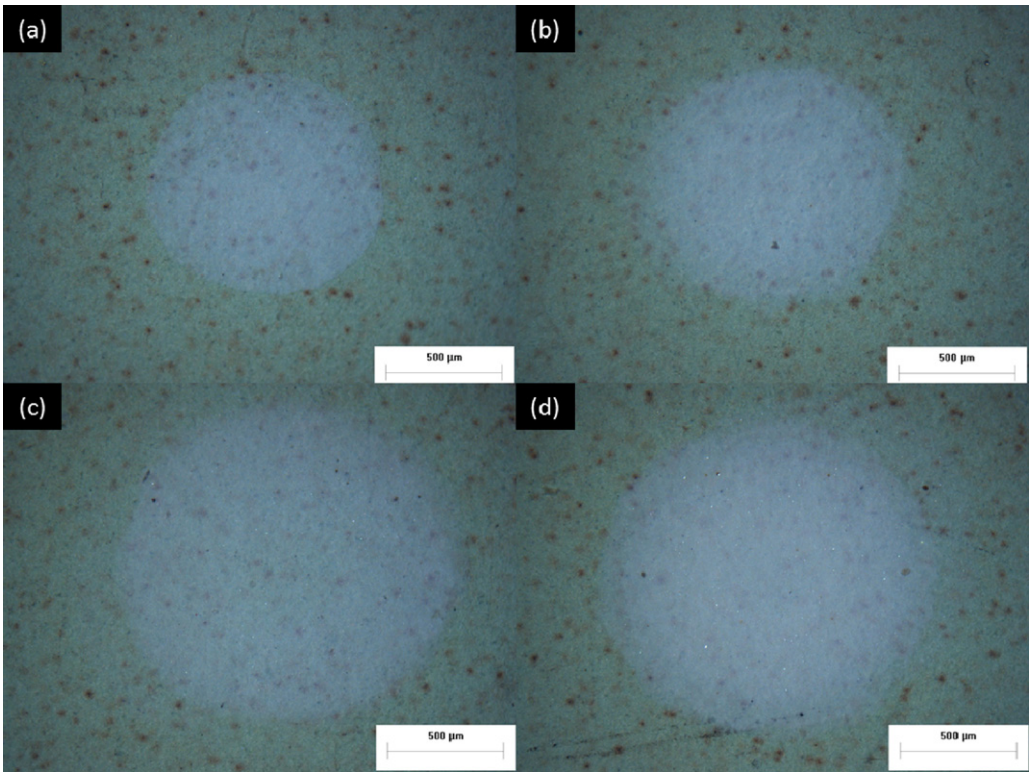

Fig. 6. Optical microscope images of drops from (a) inktm55, (b) inktm46, (c) inktm37 and (d) inktm28. Scale bar is 500 μm.

introduced, and the drop detached from the orifice after around 1400 μs. After this time, the droplet volume and velocity both remain constant.

Coalescence of the ink stream in to a single drop within 4.6 mm of the nozzles was only possible for pressures above 400 mbar and opening times in the interval of 450–550 μs. This range is defined as the stable printing regime. Within this regime, the drop volume varied from 8 nL to 20 nL depending on the pressure and opening time. The drop volume is influenced by both the printing pressure and opening time, but the dependence of the opening time was more pronounced as shown in Fig. 4. On the other hand, the velocity of the drop is also influenced by both pressure and opening time, but the dependence on opening time is much less pronounced in the tested range. The velocity of the drop is approximately proportional to the printing pressure within the experimented range as shown in Fig. 5, as the ink pressure provides the force required during the jetting process.

Since the drop volume influences the printing resolution and the thickness which can be achieved, the printing parameters that yield the minimum drop volume is selected, since the primary objective for the target SOFC application is making a dense thin film. Within the stable jetting regime, it was found that the combination of 400 mbar and 450 μs yields the smallest drop volume over the tested ranges, thus being most suitable for thin film fabrication. The drop volume is approximately 8.6 nL. The fluctuation in estimated drop volume (less than 5% of the total volume) is caused by the uncertainty arising from image thresholding, image resolution and the volume calculation procedure (which assumes ideal rotationally symmetrical drops). After the ink stream is detached from the nozzle plate, the ink velocity remains constant. The maximum velocity achieved in this case is around 2.2 m/s. The velocity in general influences the effective printing resolution and the maximum acceptable printing speed, particularly for small drops in a production environment; but this value is adequate for the printing conditions used in the present work.

3.3. Deposited relic

All inks were deposited on porous substrates in order to investigate the uniformity of the deposited drop relics. Fig. 6 shows the deposited drop relics for each ink. All samples appear to exhibit a uniform deposition of particles, even for the mixture with very high methanol content (Inktm28) which is most likely to display the non-uniform thickness arising from the coffee staining effect due to the high evaporation rate. The absence of this effect in all the samples can be explained by considering the relative timescale of three processes simultaneously occurring after drop impact. There are three identified processes occurred simultaneously: capillary draining due to the porous substrate, evaporation from the perimeter of the drop and Marangoni flow (which opposes the evaporation-driven outward flow).

An indication of the timescale on which each process occurred was obtained using the drop visualisation camera system. The time taken for capillary draining was estimated by continuously imaging the substrate during and after the impact of a drop of the ink. A series of photographs were taken from the time drop ejection was triggered at 30 frames per second and, by counting the number of frames (each frame was 33 ms apart) from drop impact until the liquid was completely drained, the

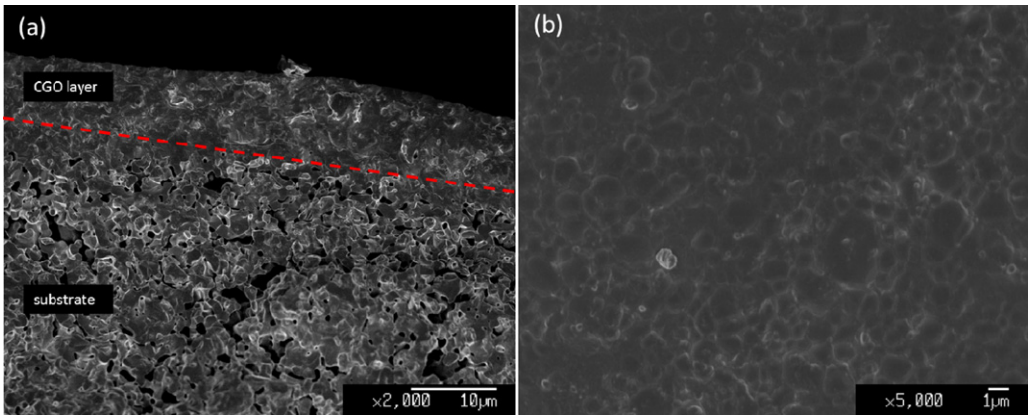

Fig. 7. Secondary electron image o of Pt coated CGO film after sintering at 1400 °C for 4 h in (a) cross-section and (b) top views.

capillary draining time was estimated. Similarly, the time taken for evaporation to complete was estimated in a similar manner by printing inks and pure methanol on a glass slide. It was assumed that the Marangoni flow occurs on a similar timescale to evaporation, since Marangoni is an opposing force to evaporation flow so that it only exists when evaporation flow is present.

It was found that the ink was completely drained within 200 ms by capillary draining, whereas the evaporation of inktm28 was incomplete even after 3 min. Capillary draining was orders of magnitude faster than evaporation. Therefore, capillary draining was considered as the dominant process, which implies that both evaporation and Marangoni flow have insufficient time to occur. The result suggests that coffee stain formation is not an issue on a thick porous substrate where capillary draining can take place.

It is also noticeable that the diameter of the deposited drop increased as the methanol content increased, i.e. a drop from inktm28 is 25% larger in diameter than one from inktm55. This is attributed to the low viscosity of methanol which allows the spreading of the drop. Surface tension may also be a contributed factor since methanol has low surface tension (22.6 dyn/cm) value compare to terpineol (31 dyn/cm) which also alter the drop speared behaviour.[11] Depending on the application, the methanol content could be varied within the stability limits to tailor the ink rheology. For instance, if one requires high resolution printing, the methanol content should be kept low to avoid spreading and vice versa.

As shown in Fig. 6, all drops are quite similar in terms of circularity and shape. However, the ink edges smudge as the methanol content increases due to more favourable ink spreading, which may be undesirable if printing well-defined features such as tracks is required. In summary, all inks produce uniform deposits on this porous substrate, but the methanol content should be kept to the minimum necessary to obtain high resolution printing while achieving an ink which was printable at a reasonable working pressure.

Finally, printing of a dense film was achieved on a porous substrate as shown in Fig. 7. The CGO film appears to be dense without any open or closed porosity after sintering. The high density of the film can be attributed to the capillary force which compacts the ceramic powder in its green state during drying.

4. Conclusions

It has been demonstrated that stable ceramic suspensions with suitable rheological properties for inkjet printing can be successfully produced. The ink contains three components: the solvent (liquid carrier), functional oxide particles and a polymeric dispersant. The composition of the solvent mixture was found to be the most critical part of the ink formulation as it influences both the rheological properties and the stability. It was found that a 50:50 vol% mixing ratio of terpineol and methanol was the optimum ratio as it satisfied all the criteria required (ink stability, printability and drop integrity). No coffee staining was observed on that sample as capillary draining impedes the evaporation flow which is the driving force for coffee staining ring formation. Nevertheless, the composition may still affect the spreading mechanism of the drop, which influences the uniformity especially if the substrate is not porous. The stable printing regime for the CGO ink (inktm55) was found to be in the range of 400–800 mbar and 550–600 μs for printing pressure and nozzle opening time respectively. Within the tested range the drop velocity is determined by both the printing pressure and the opening time, while the drop volume is predominantly determined by the opening time. Depending on the requirements, one could optimise the parameter combination within the stable printing regime (e.g. for high resolution printing, select the lowest pressure and opening time). For ink inktm55, a pressure of 400 mbar and a 450 μs opening time yields the smallest droplet size, which is most suitable for thin membrane fabrication. The corresponding ink volume and velocity are 8.6 nL and 2.2 cm/s, respectively. The ink formulation and printing approach described in this paper can also be applied to several different technologically interesting oxides (the authors have tested YSZ, NiO and CGO, please refer to electronic annex), which could accelerate the widespread development of inkjet printing as an alternative membrane fabrication technique.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2012.03.001.

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