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Ink formulation and printing of electrolyte for a doped ceria solid oxide fuel cell

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ABSTRACT

We propose a simple ink formulation and a rapid preparation technique to deposit a 20 mol% gadolinium-doped ceria electrolyte utilizing nanopowders and a polymeric dispersant. The ink was assessed for printability and was successfully printed using a piezoelectric inkjet materials printer. The ejected drops were investigated using built-in stroboscopic imaging during ejection, and the deposited thin films were characterised using optical microscopy and surface profilometry. Inkjet material deposition provides a highly repeatable process for the fabrication of solid oxide fuel cells (SOFCs) that can be up-scaled to industrial levels.

1. Introduction

Solid oxide fuel cell (SOFC) devices are capable of addressing low-carbon emission targets by providing the generation of heat and power whilst utilizing low-carbon, renewable sources (green hydrogen) with low-waste output (water). The development of these devices is hindered by high material costs and device degradation. Inkjet printing is a non-standard SOFC manufacturing technique which can address high material costs by reducing the required input material whilst providing high process reproducibility and speed compared with other SOFC manufacturing techniques, such as tape casting, nanolithography and atomic layer deposition techniques [1,2].

High operational temperatures (1000 °C) contribute to SOFC degradation and so, lower operational temperature SOFC materials are sought, such as Intermediate-temperature (IT) – SOFCs operating at 600 °C. A highly conductive (0.1 S/m) IT-SOFC material is gadolinium-doped ceria which constitutes the electrolyte component within SOFC, providing high ionic conductivity [3].

To ensure high quality jetting of SOFC inks piezoelectric printers are well-suited owing to the high programmability of the cartridge's ejection voltage-waveform [4,5]. This combined with proper adjustment of the size of the solid particles suspended in the ink, will prevent nozzle clogging and will allow for uniform printing [6]. Additionally, the selection of a suitable ink dispersant will prevent the aggregation of the solid particles in the ink suspension, thus ensuring long-term ink stability [7]. Polyvinylpyrrolidone (PVP) is a suitable candidate, an amphiphilic dispersant that is non-toxic to the environment, and also acts as a complexing and wetting agent [8].

In this work a simple and cost-effective 20 mol% gadolinium-doped ceria (20GDC) electrolyte ink for IT-SOFC was formulated based on a hybrid aqueous ethanol blank solvent complex (water as a solvent and pure ethanol as co-solvent) for a PVP dispersant. The resulting blank ink was solid-loaded with a 20GDC nanopowder in different concentrations and ejection and printing was demonstrated.

2. Materials and methods

Absolute ethanol 99.8 % (Fisher Chemical) was added to PVP powder ~10,000 MW (Sigma-Aldrich) in a beaker while manually shaking. De-ionised water of resistivity 17 MΩ.cm was then added to the beaker while stirring vigorously using a stainless-steel spatula. The content of the beaker was then transferred back and forth in another empty beaker until a clear yellowish solution was obtained. While preparing the blank ink solutions, the volume of de-ionised water was kept constant at 25 mL, while ethanol was added at 16 w/v% of the mass of PVP to ensure proper wetting of the PVP powder. Table 1 shows the PVP solution series that was prepared for the assessment of printability.

To assess the printability of the prepared solutions, the density, viscosity, and surface tension of each solution were measured at 20 °C using the Ohaus Explorer EX225DM balance, Anton Paar ViscoQC 300 viscometer equipped with their PTD 80 temperature controller and DG26 measuring system, and Kruss EasyDrop respectively. The Z-number is taken as an indicator for the printability of the ink [7], where,

$$Z = \frac{\sqrt{\rho \gamma d_n}}{h} \tag{1}$$

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Table 1
The formulation of each solution in the prepared PVP concentration series.

Constituent	Amount					
PVP Concentration (w/v%)	2	5	7.5	10	15	20
Mass of PVP (g)	0.5	1.25	1.875	2.5	3.75	5
Volume of Water (mL)	25	25	25	25	25	25
Volume of Ethanol (mL)	3.1	7.81	11.7	16	23.4	31

where ρ is the density, γ is the surface tension, d_n is the nozzle diameter, and h is the viscosity. The nozzle diameter of the printer used is 21.5 µm and the Z-number should be between 1 and 10 for a printable ink [4].

The solid-loaded ink was prepared by adding 20 mol% gadolinium-doped ceria nanopowder (Sigma Aldrich) to the 20 w/v% PVP solution to obtain inks with solid concentrations of 0.1 w/v%, 0.2 w/v%, 0.5 w/v%, 1 w/v%, and 10 w/v%. Each prepared ink was sonicated in a water bath and then stirred, with the process repeated for a total of 90 min. Filtration using Whatman polyethersulfone (PES) 0.2 µm syringe filters was then attempted on all prepared inks where it failed for 1 w/v % and 10 w/v% inks and succeeded for the other three concentrations. Nanoparticle tracking analysis (NTA) using NanoSight LM10 was then used to determine the mean particle size and the solid particle concentration in the filtered ink.

The Dimatix DMP-2831 (Fujifilm) piezoelectric inkjet materials printer equipped with DMC-11610 cartridge (21.5 µm nozzle diameter, 10 pL drop volume) was employed to test the printability of the blank ink and to print solid-loaded filtered inks on sacrificial alumina substrates. Before printing, the substrates were thoroughly cleaned using isopropanol and acetone. The printer cartridge was filled with 1.5 mL of the ink and its temperature was adjusted at 28 °C, while the platen temperature was adjusted at 45 °C. The drop spacing was set at 5 µm to obtain a dense film and two layers were printed. Maximum jetting speeds that produced drops without satellites were obtained by adjusting the jetting voltages of the nozzles in the range 14.5 V to 16.5 V.

Keyence VHX-1000 optical microscope and JEOL JSM-7400F SEM were utilized to inspect the surface features of the printed thin films, and Bruker DektakXT stylus profilometer was used to estimate the average thickness of the sintered and un-sintered printed films.

3. Results and discussion

Fig. 1 shows the variation of the density, viscosity, surface tension, and the Z-number of the blank ink with the PVP concentration. The Z-number was calculated from Eq. (1).

Fig. 1 shows that the Z-number decreases with increasing PVP concentration. A PVP concentration of 20 % has the Z-number of 5, which is within the printability range. Thus, the 20 % solution was selected as the most suitable candidate for printing.

Failure to filter the high solid loading inks (1 and 10 w/v%) is attributed to the formation of agglomerates larger than 0.2 µm in size even after sonication and stirring.

Keeping the mean particle size within 200 nm is essential to prevent clogging of the printing nozzle and the formation of aggregates, thus maintaining the stability of the ink. The median (D50) particle size of the filtered inks was found to be 144.1 ± 22.3 nm. The solid particle concentration was found to be nearly constant at 3.45 × 10^8 particles/mL across all tested ink concentrations. This important finding signified that

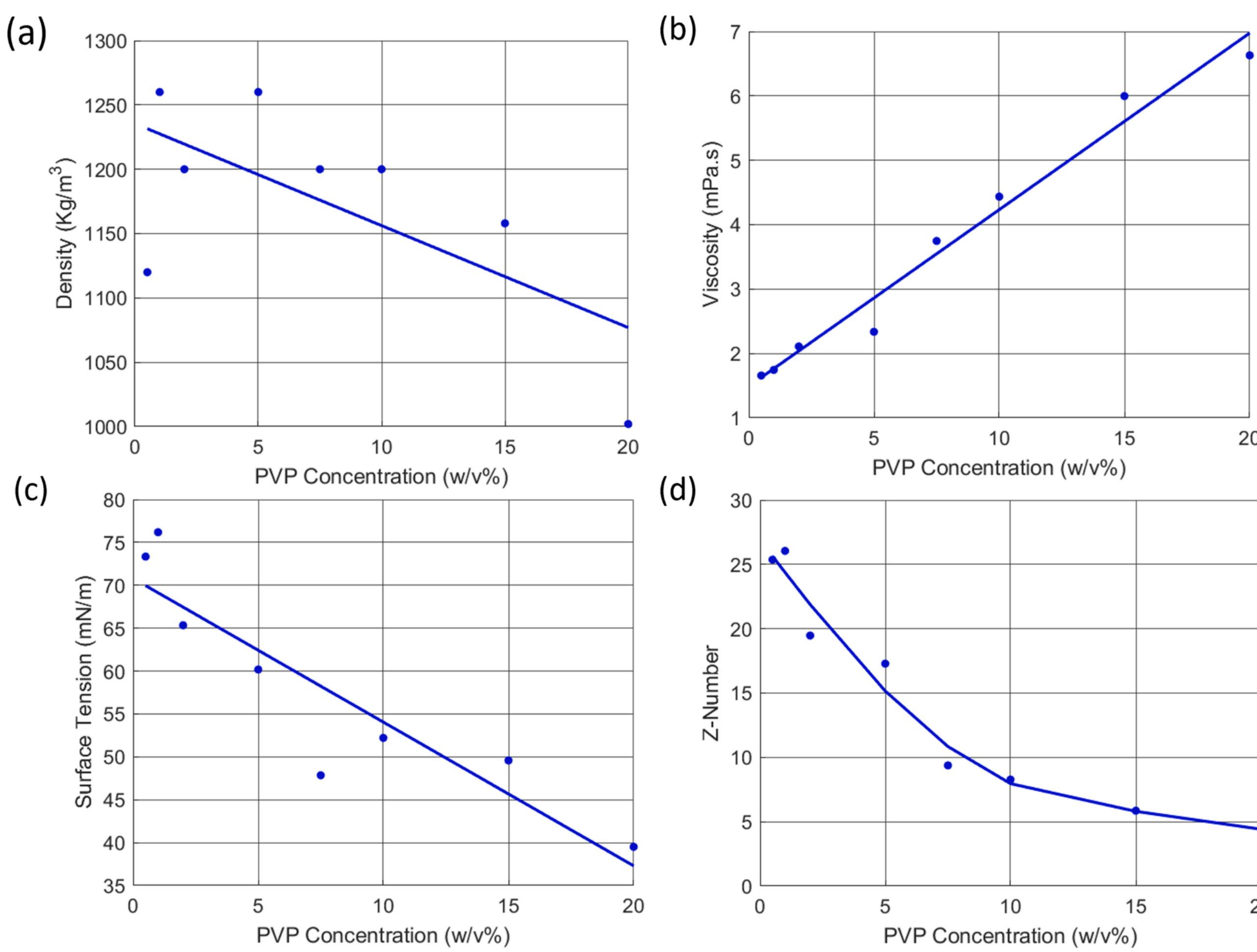

Fig. 1. The variation of (a) the density, (b) the viscosity, (c) the surface tension, and (d) the Z-number with the PVP concentration.

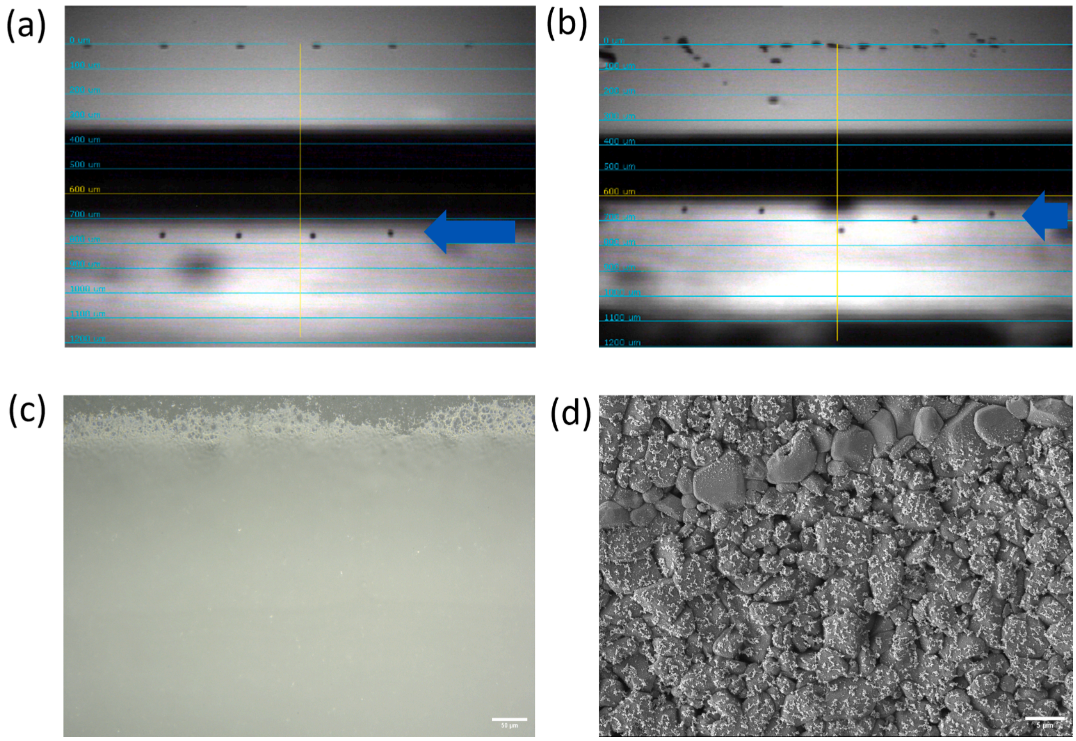

Fig. 2. (a), (b) Stroboscopic 100 μs images showing ejected drops in-flight (by arrows) for the blank and solid-loaded inks respectively. (c) A top-down optical microscope image for the electrolyte thin film printed on an alumina substrate. (d) Microstructure of electrolyte deposit by SEM.

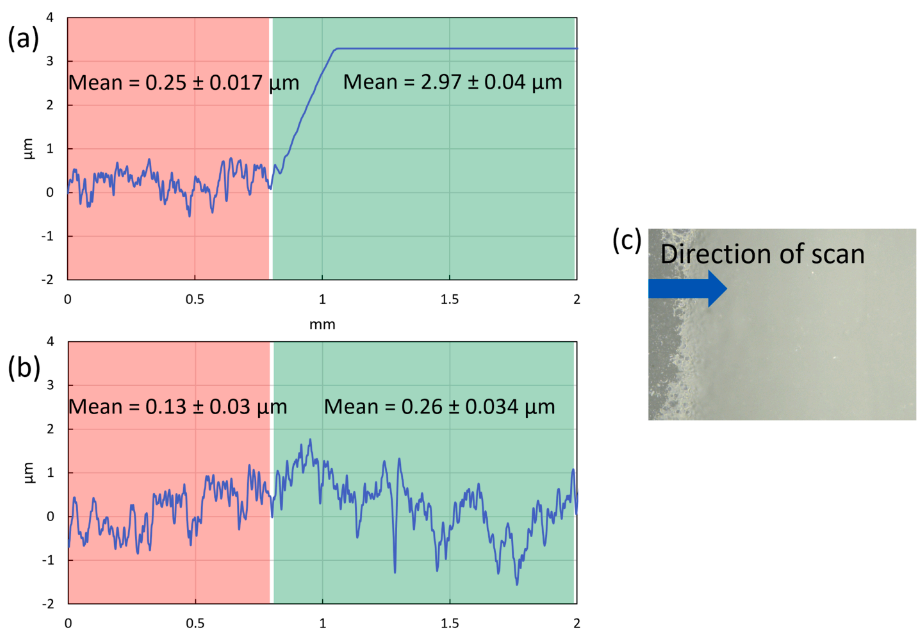

Fig. 3. Surface profiles of (a) un-sintered, and (b) sintered printed thin films. (c) shows the direction of profile scan from the substrate (in red) onto the printed film (in green). The thickness is taken as the difference between average profiles of the two regions.

the filtration process results in a constant solid loading in the ink regardless of the prepared concentration of the unfiltered ink.

The Z-number of the filtered ink was calculated according to Eq. (1) and was found to be equal to 4.98. This indicates that the filtered ink is printable and that the addition of the 20GDC nanopowder to the blank ink does not significantly change its Z-number.

Fig. 2(a) (blank ink) and (b) (solid-loaded ink) are stroboscopic 100 μs taken by a built-in digital CCD camera to demonstrate the shape of the ejected drops and to calculate their speed. As can be seen, the ejected droplets (by highlighted arrows) are perfectly round and are without satellites. The speed of the ejected drops is in the range of 6.5 m/s to 7.5 m/s, which is indeed in the optimal range for materials inkjet printing [9].

Fig. 2(c) and (d) show the surface features of the printed films using optical microscopy and SEM respectively. Here, the surface morphology reflects a dense electrolyte film after sintering.

Fig. 3(a) shows that the surface profile of the un-sintered film has an average thickness of 2.72 ± 0.023 μm. Fig. 3(b) shows the profile of the sintered film has an average thickness of 130 ± 4 nm. The polymeric dispersant (PVP) in the un-sintered film provides a significantly smoother surface than that of the sintered film where all non-solid components have disintegrated and only the solid 20GDC remains.

4. Conclusion

A cost-effective ink with a relatively simple composition was formulated from safe and environmentally friendly substances. It is demonstrated that the ink can be rapidly prepared to inkjet print gadolinium-doped ceria (GDC) as an electrolyte for solid oxide fuel cell (SOFC) applications. The ink utilized Polyvinylpyrrolidone (PVP) as dispersant and surfactant with an average Z-number of 5, hence indicating good printability of the ink. The concentration of GDC in the ink was found to be constant after filtration regardless of the amount of GDC added to the blank ink before filtration. The formulated ink jetted successfully, and optical microscopy and surface profilometry showed that the printed thin films are of good quality. This paves the way for inkjet printing the electrodes and functional layers of a full SOFC in the near future.

CRediT authorship contribution statement

Mohamed Ahmed: Conceptualization, Methodology, Data curation, Writing – original draft. **Thomas D.A. Jones:** Methodology, Investigation, Writing – review & editing, Supervision. **Amin Abdolvand:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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