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Ink-jet printing of Cu-Co-Mn Oxide spinel as protective coating on solid oxide fuel cell interconnects

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Abstract

In the present study, ink-jet printing was used to deposit layers of Cu-Co-Mn-oxide. The advantage of the technique lies in the flexibility of the coating design, low fabrication cost and the very low amount of wasted material.

Cu-doped $MnCo_2O_4$ spinel nanoparticles were produced in house via the Pechini method. The material was characterized with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Particle Size Analysis (PSA) and Thermogravimetric Analysis (TGA). The present study focuses on the preparation of a stable, well-dispersed and agglomerate-free particle dispersions that will be subsequently tuned as ink. Ink composition and printing parameters were optimized to obtain high-resolution printing. To assess these properties, stability, viscosity and the surface tension were measured for the ink and droplet interpolation, jetting frequency for the printing process. The printable ink was deposited on an interconnect steel substrate and then cured at 600°C.

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Introduction

The degradation of ferritic stainless steel (FSSs) interconnects is one of the main issues in Solid Oxide Fuel Cells (SOFCs). The chromium oxide thermally grown on the steel surface causes ohmic losses and its vapors poison the cathode perovskites.

In order to prevent cathode poisoning, protective coatings are an established solution, with spinel oxides being the most employed materials. Regarding the coating deposition technique there is a choice of methods, with those leading to good performance like PVD being counterbalanced by the deposition cost. Interest in rapid prototyping has increased dramatically in recent years, where Ink-Jet Printing (IJP) in particular is studied for the deposition of thin films. IJP is attracting interests due to its high resolution, low-cost, simplicity, contactless process, feasibility to use for a wide range of materials/substrates, possibility to use for large scales, and low material waste.

Depending on the printing mechanism, an ink-jet printer can be operated in two different modes: continuous ink-jet (CIJ) and drop-on-demand (DOD) printing. The DOD mode is a process in which droplets are jetted only when desired. Thermal and piezoelectric actuations are the two main actuation mechanisms of a DOD inkjet printer [1]. In the piezoelectric process, a voltage pulse is applied to the piezoelectric elements placed on the ink reservoir walls, which creates a mechanical pressure. The pressure squeezes the functional ink through the nozzle generating a droplet [1].

The objective of this study is to use drop-on-demand ink-jet printing to deposit a thin film of Cu-doped $MnCo_2O_4$ spinel on ferritic stainless steel K41 (the SOFC interconnect substrate) as protective coating. The powders were synthesized using the Pechini method [2] and then characterized. The ink formulation and printing process will be subsequently explained in detail. The operating printing parameters were studied: substrate/printhead temperature, drop spacing, jetting waveform, applied voltages to the nozzles, substrate/printhead distance, and number of nozzles to achieve a qualified printing layer.

Material and Experiments

Powder synthesis

The Pechini method was used to synthesize $Mn_{1.4}Co_{1.4}Cu_{0.2}O_4$ nanoparticles. Considering the desired stoichiometry, proper amounts of $Mn(NO_3)_2.4H_2O$, $Co(NO_3)_2.6H_2O$, and $Cu(NO_3)_2.3H_2O$ (all from Sigma Aldrich) were dissolved in a mixture of distilled water and ethylene glycol which was then stirred to a homogenous solution. Citric acid was added during stirring and heating up to 70°C. The solution was finally stirred at 150°C for one hour. In this stage a viscous gel is obtained. The gel was dried at 250°C for 2 hours, and the dried gel calcined at different temperatures (500°C, 550°C, 600°C and 800°C).

Ink preparation

A successful ink-jet printing process is linked to the proper adjustment of (i) the physicochemical properties of the ink (mainly viscosity, surface tension, and solubility/dispersibility of the material to be printed), (ii) printing parameters (e.g., piezoelectric actuation), (iii) ink–substrate interaction (wetting behavior), and (iv) post-processing (to convert the ink after drying into a solid functional material) [3].

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A suitable solvent for the ink should meet requirements for the printing. In terms of surface tension, too low surface tension leads to spontaneous ink dripping from the nozzles, while too high values make jetting impossible [4]. The dynamic viscosity affects the shape, size and velocity of the ejected droplets and is a crucial physical parameter of the ink [5]. The printability of an ink can be checked using the inverse of Ohnesorge number (Z) [6], defined as $Z = 1/Oh = \sqrt{\gamma\rho\alpha}/\eta$ where γ, η, ρ, and α are the surface tension, viscosity, density of the ink, and characteristic length (here the nozzle diameter with α =21.5 μm), respectively.

Rapid drying of the solvent is another issue which may also cause blocking of the nozzles [1] or produce a non-uniform layer due to the change in substrate/ink interaction. This phenomenon may be suppressed by using cosolvents that dry relatively slowly [1]. Based on the mentioned points, a mixture of 1,2 propanediol (95%, Sigma Aldrich), isopropanol and water were found to meet the criteria as solvent. Amounts of 4 mg spinel nanoparticles were added to 2 mL solvent and then dispersed with ultrasound for 120 minutes at 60% amplitude with on/off circle of 5s. The prepared ink was then characterized. The viscosity was measured by SV-1 A series viscometer (A&D, Japan) to a value of 5.96 mPas at 25 °C. The surface tension was measured using Drop Shape Analyzer DA30 S (Krüss, Germany), equal to 31.22 $\pm$1 mN·m^{-1}. Then, the Z parameter was obtained as 4.09, which is within the acceptable range of $1<Z<10$ [6].

The other bottleneck of ink-jet printing is to avoid nozzle blocking due to particle agglomeration. The size of the particles in an inkjet ink should be at least two orders of magnitude smaller than the diameter of the nozzle orifice in the printhead to prevent clogging and nozzle blockage [7] Roll milling was used to control particle size in order to avoid nozzle clogging during printing.

The stability of the ink is referred to as non-agglomerated and non-sedimented ink. Here, the agglomeration of the ink was checked by Dynamic Light Scattering (DLS), (model: ZetaSizer Nano ZS, Malvern, UK), in which the particle size was measured after certain elapsed times. The DLS measurement of the ink showed the same distribution at different standing times up to 30 hours, which indicates no detectable agglomeration of the particles. Although the 30 hours of stability was proper for printing, while polyvinyl pyrrolidone (PVP; MW 10′000, Sigma-Aldrich) additive was used to improve ink stability for long-term usage.

Printing

In piezoelectric drop on-demand (DOD) inkjet printing, a pulsed voltage is applied to the piezoelectric actuator which causes piezoelectric crystal deformation; the generated stress results in droplet formation. Hence, the applied waveform is effective on the droplet shape. Drop spacing is an important factor during printing which is defined as the distance between the center of two adjacent droplets on the substrate and can greatly affect film surface coverage [7]. If drop spacing is either too large or too small then it can cause a non-uniform and low resolution layer. Inkjet printing was performed using a Dimatix DMP-2850 inkjet printer equipped with disposable cartridges containing 16 nozzles with 10 pL nominal droplet volume, 254 μm spacing and 21.5 μm in diameter.

The suitable drop spacing for the prepared ink to print on stainless steel K41 was optimized as 35 μm. A single nozzle was used for printing to get higher resolution. The printhead was adjusted on a distance of 1mm from the substrate. The operating temperature was also optimized. Both printhead and substrate/stage were heated to 40°C and 60°C respectively. Then the sample was thermally cured at 600°C for 1 hour.

Results and discussion

$Mn_{1.4}Co_{1.4}Cu_{0.2}O_4$ nanoparticles were synthesized using the Pechini method. Structural characterization was checked on a D8 Advance Bruker X-ray diffractometer (XRD) with Cu-Kα radiation source.

Fig.1 displays XRD patterns of Cu-doped $MnCo_2O_4$ spinel powders at different calcination temperatures: 500, 550, 600, 800°C. The XRD pattern of the non-calcined powder is showing that the crystalline phase is not formed yet. It seems that the cubic spinel phase is formed after calcination at 500°C. It is obvious that there is a phase transition between 500°C and 550°C. The reference lines of the cubic and tetragonal $MnCo_2O_4$ spinel in Fig.1 confirm the phase transition from cubic to tetragonal crystalline phase. The cubic spinel can be identified by nine peaks which can be respectively assigned to the diffraction lines produced by the (111), (220), (311), (222), (400), (331), (422), (511) and (440) planes of $MnCo_2O_4$.

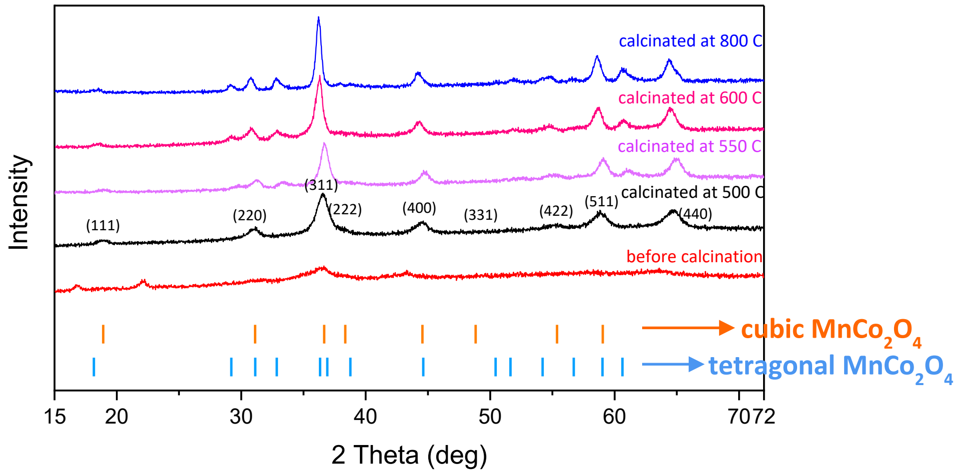

Fig.1. XRD patterns of synthesized $Mn_{1.4}Co_{1.4}Cu_{0.2}O_4$ nanoparticles at different calcination temperature

Comparing tetragonal spinel patterns, it is found that by increasing calcination temperature the dominant peak at around 36° is getting sharper which means the crystalline quality is improving. This can be also confirmed by SEM images (Fig.2) in which the crystalline facets can be easily distinguished for the powder calcined at 800°C. Later, it is shown that the particle size measured by DLS is in agreement with SEM images.

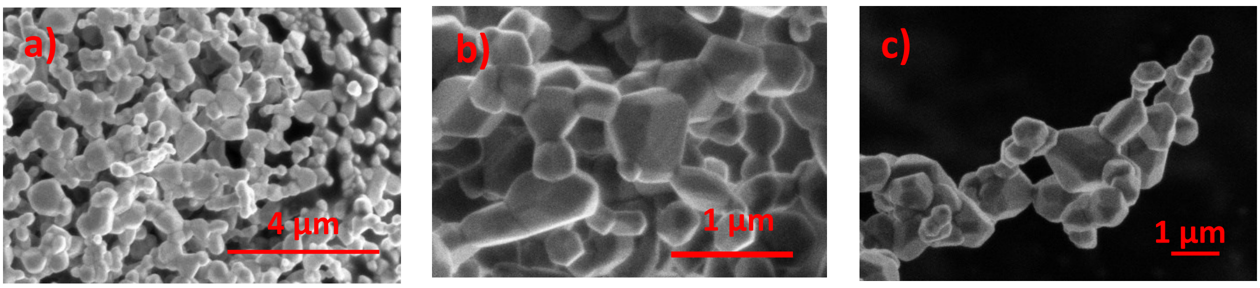

Fig.2. SEM images of the synthesized $Mn_{1.4}Co_{1.4}Cu_{0.2}O_4$ nanoparticles via the Pechini method (and calcined at 800° C)

Thermogravimetric analysis (TGA) was performed on around 8 mg of spinel powder using alumina crucibles (Fig.3). The mass change was recorded between room temperature and 900°C in flowing air (20 mL/min) at 10°C/min heating and cooling rates. Measurement was performed for the samples calcined at different temperatures. It is observed that the weight change is largest for the sample which was calcined at 400°C followed by the one calcined at 500°C. Considering these two powders, the weight loss in the first 200°C come from water evaporation and at higher temperatures can be the result of impurity removal and the cubic/tetragonal phase transformation. The powders calcined at 600°C and 800°C show more stable trends, since the higher calcination temperature already removed the impurities. It can be concluded that the spinel powders calcined at 600°C and 800°C are stable at high temperature. Hence, the Cu-doped $MnCo_2O_4$ synthesized powder was selected to use in ink-jet printing.

As described in the previous section, particle size is one of the key parameters in ink-jet printing. Particle size can be controlled within the last two steps of the Pechini synthesis

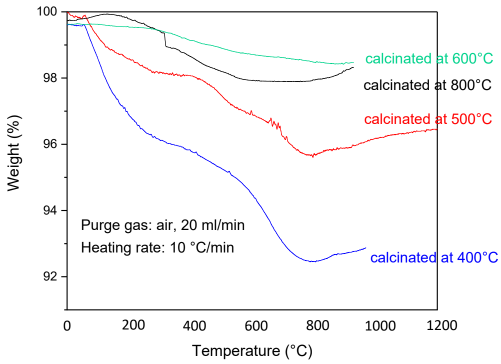

Fig.3. Thermogravimetric analysis of Cu-doped $MnCo_2O_4$ powder and the weight change as a function of temperature

process: milling and the calcination temperature/ramp (the schematic of the method is displayed in Fig.4a). Figs.4b & 4c show the particle size distribution before and after milling. DLS measurement (Fig.4b) showed that as-synthesized particles' size (non-milled particles) were on average in the range of 340 nm. Although this was still acceptable for printing, particles were milled further to control the size and obtain a homogeneous powder in order to improve the ink quality and to avoid agglomeration and nozzle clogging. Fig.4c displays nanoparticle size distribution after using roll milling, in the range of 200nm. Milling was performed before calcination; otherwise, if it is performed after crystalline formation, it may destroy powder crystallinity. Fig.4d shows an image of the formulated ink, and in Fig.4e the surface tension measurement of the ink is observed.

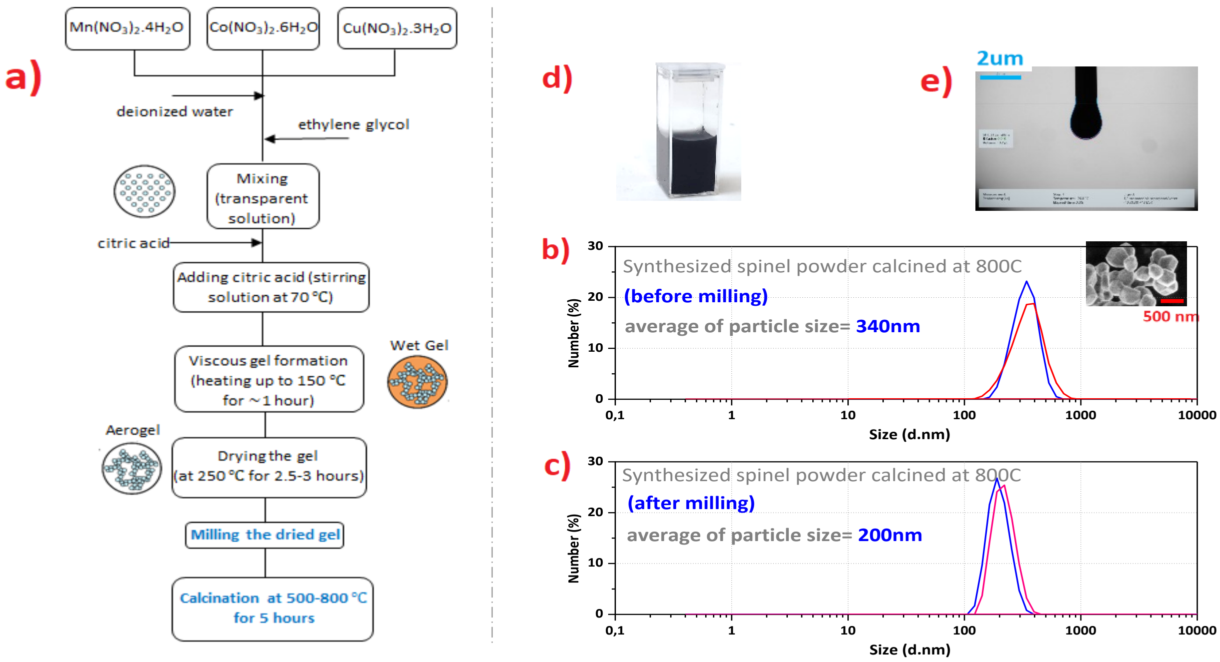

Fig.4. a) Schematic of Pechini process used to synthesize Cu-doped $MnCo_2O_4$ spinel powders, b) particle size distribution of the non-milled synthesized powder calcined at 800°C, c) particle size distribution of the synthesized powder after milling and then calcined at 800°C, d) an image of formulated ink, e) surface tension measurement of the ink using pendant drop method

The formulated ink containing milled synthesized particles (calcined at 800°C) was used for DOD ink-jet printing, with the schematic displayed in Fig.5a. On the jetting waveform, we can control the shape of the pulse to the nozzle to eject the droplets. Fig.5b shows the applied waveform which creates the pulsed voltage on the piezoelectric and then the piezoelectric deformation results in drop formation. Thus, it makes sense that the drop shape is highly dependent on the jetting waveform, ink surface tension and viscosity. If jetting waveform is not appropriate or if the properties of the ink are not meeting criteria, then the single droplet may not form. In this case, the droplets may eject with satellites or tails, which decrease the printing resolution and will deposit a non-uniform layer. In Fig.5e different drop formations are shown as the result of different nozzle voltage. From right to left (in Fig.5e) voltages of 14-26V were applied to the nozzles at the same time. The formed droplets show that the higher the voltage applied, the faster the drop formation. The tail effect is dominant at higher voltages. A satellite droplet is also observed applying 16V to the nozzle. So here the nozzle with 14V applied voltage is the only case which formed a single droplet. In Fig.5c & 5d, the drop formation from the nozzles with 14V and 22V applied voltages are compared in detail. The drop formation is shown with elapsed time intervals, in which the tail effect and the single droplet can be found for the nozzles with 14V and 22V respectively. On the other hand, it should also be considered that too low voltage can be insufficient to eject the droplet and clog the nozzles. The results were obtained in the state of substrate and printhead heating up to 60°C and 40°C, respectively. It should be noted that temperature also affects the drop shapes (because viscosity is temperature-dependent), and a small change in temperature may form different droplets at the same mentioned applied voltage.

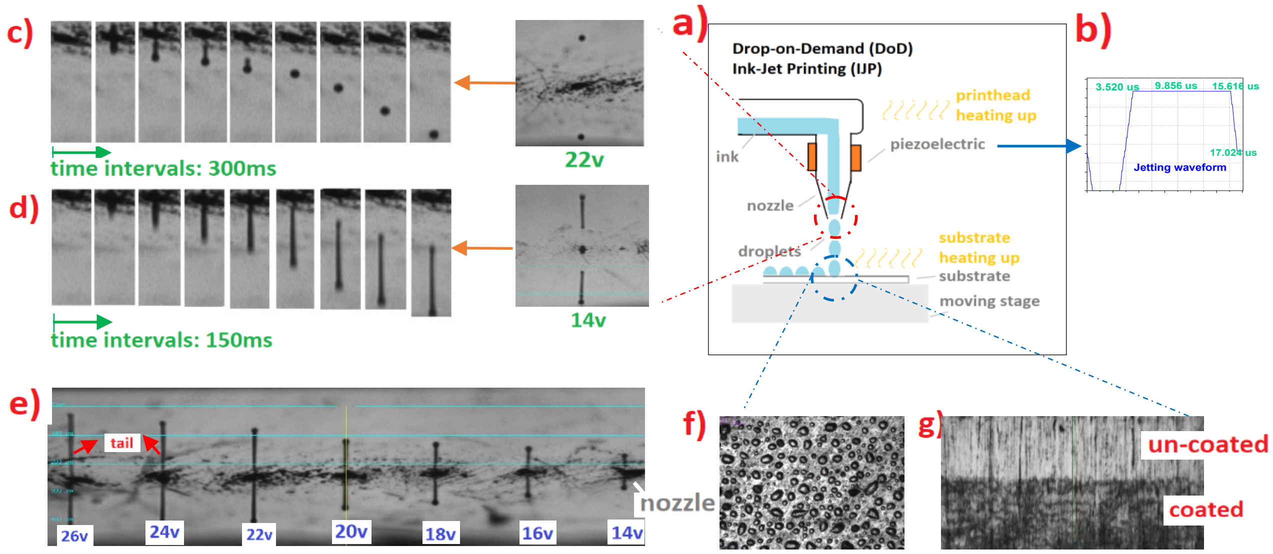

Fig.5. a) Schematic of DoD ink-jet printing with piezoelectric actuator, b) pulsed jet applied to the nozzle, c) drop ejection from a nozzle with applied 22V in different time intervals, d) drop ejection from a nozzle with applied 14V in different time intervals, e) satellite and tail effects of droplets using different jet frequencies, f) non-ideal drop spacing (large spacing), g) printed layer of $Mn_{1.4}Co_{1.4}Cu_{0.2}O_4$ spinel powders on stainless steel K41

Drop spacing is also one of the key parameters to print a uniform layer, as explained above. It highly depends on the ink-substrate interaction and ink properties itself. So, the drop spacing should be optimized for any specific ink. Here, 35µm was found to be the optimum spacing. The short drop spacing causes drop overlaps and the large spacing results in a non-uniform printing (Fig.5f shows a case of a large drop spacing). Finally, based on the mentioned operating parameters, the formulated ink was printed.
on the substrate and then thermally cured at 600°C for one hour. Fig.5g shows a printed sample , and film characterization will be performed next.

Conclusion

$Mn_{1.4}Co_{1.4}Cu_{0.2}O_4$ spinel nanoparticles were synthesized using the Pechini method and characterized. The purpose is to coat a spinel layer on SOFC interconnects (stainless steel K41) as protective layer in terms of chromium mitigation using the ink-jet printing method. A printable ink was formulated in which the synthesized powders were dispersed. First printing was performed using the formulated ink. The following points are drawn as conclusion:

- Calcination temperature for the synthesized powder was optimized. Based on the results, the sample calcined at 800°C showed more qualified crystallinity.
- Different solvents were studied and a mixture of 1,2 propanediol, isopropanol and water including Cu-doped $MnCo_2O_4$ with 200nm average size was considered as ink for printing.
- Polyvinyl pyrrolidone (PVP) additive was used to improve ink stability for long-term usage and to obtain a well-dispersed and agglomerated-free ink.
- The Z parameter (printability factor) was obtained as 4.09, which is within the acceptable range.

- The operating printing parameters were optimized: substrate/printhead temperature, drop spacing, jetting waveform, applied voltages to the nozzles, substrate/printhead distance, and number of nozzles for printing.

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