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# Green fabrication of composite cathode with attractive performance for solid oxide fuel cells through facile inkjet printing

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## HIGHLIGHTS

- The cathode layer was fabricated by inkjet printing.
- The cathode layer was based on environmentally friendly water-based ink.
- A pore former was introduced into the cathode ink.
- High power and OCV were obtained for the cell with cathode preparation by inkjet printing.

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## ABSTRACT

The inkjet printing technique has numerous advantages and is attractive in solid oxide fuel cell (SOFC) fabrication, especially for the dense thin electrolyte layer because of its ultrafine powder size. In this study, we exploited the technique for the fabrication of a porous SDC/SSC composite cathode layer using environmentally friendly water-based ink. An optimized powder synthesis method was applied to the preparation of the well-dispersed suspension. In view of the easy sintering of the thin film layer prepared by inkjet printing, 10 wt.% pore former was introduced to the ink. The results indicate that the cell with the inkjet printing cathode layer exhibits a fantastic electrochemical performance, with a PPD as high as 940 mW $cm^{-2}$ at 750 °C, which is comparable to that of a cell prepared using the conventional wet powder spraying method, suggesting a promising application of inkjet printing on electrode layer fabrication.



## 1. Introduction

Innovative technologies that can lead to increased efficiency and reduced impact on environment during energy utilization are always important for a sustainable development of our society. Fuel cells are an innovative technology that are reputed for their high energy conversion efficiency up to 80% and low emissions with a reduction in $CO_2$ emission of approximately 50% per kW of electricity compared with traditional power generation based on combustion engines [1–4]. A combination of solid-oxide fuel cells (SOFCs), high-temperature electrochemical energy conversion devices, with renewable biofuels, may provide a practical solution for providing clean electric power supply of the future [5–7].

The fabrication cost, material cost, cell power output, and cell lifetime are some of the important factors that largely determine the practical application of SOFC technology. Currently, the research trend on SOFCs is shifted to reduce the operation temperature from approximately 1000 °C to the range of 500–800 °C [8–19], because such a reduction could lead to prolonged cell lifetime and reduced materials cost. To obtain a high cell power output, a thin-film electrolyte configuration is often adopted in intermediate temperature (IT)-SOFCs to offset the decrease in ionic conductivity with a decrease of operation temperature [20–23]. When tape casting has been demonstrated to be a cost-effective technique for the mass production of thick anode substrates, an anode is typically selected as the substrate [24–26]. Therefore, the development of methods for economic fabrication of thin film electrolytes and cathodes becomes one of the critical points in achieving the practical application of IT-SOFCs.

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Inkjet printing is a highly attractive technique for the deposition of thin layers in a wide range of areas including electronics processing, fine ceramics, and biological culture research [27–33]. Very recently, the application of the inkjet printing technique in the fabrication of SOFCs was also well noted [34–42], as this technique has several important advantages. First, inkjet printing can be fully automated, providing easy mass production; second, the film pattern, such as the size and thickness, can be precisely controlled, ensuring high production reproducibility; third, the fabrication is non-contact without the requirement of a mask or screen, providing non-destructive fabrication.

There have been several publications available in the literature on the fabrication of SOFCs by inkjet printing to date [34–42]; however, most of the successful attempts were focused on the dense thin-film electrolyte or thin functional layers [34–39], while few reports are available on porous electrodes [40–42]. Typically, the cathode prepared by inkjet printing performed worse than that prepared by conventional slurry painting [41]. For example, Yashiro et al. attempted to fabricate a LSCF-GDC cathode using inkjet printing method using a water-based slurry and observed that the as-prepared cathode layer had a graded size distribution with respect to depth due to the effect of gravity and caused the formation of a dense surface layer, which resulted in poor gas permeation and then poor electrode performance [41]. To improve the cathode performance, an additional slurry painted layer was required [41]. However, the double-layered cathode configuration increased the fabrication cost.

Sukeshini et al. comparatively studied the anode-supported SOFCs with cathode prepared using a slurry paste and inkjet printing [40]. α-terpineol was applied as an organic solvent, and polyvinylbutyral (PVB) and butyl benzyl phthalate (BBP) and polyalkalyne glycol (PAG) were utilized as the binder and plasticizer constituents. These researchers demonstrated that the microstructure of the printed layers could be tailored by altering the rheological property of the ink and/or the printing process parameters. After optimization, the cells could deliver similar performance with the cathode prepared by hand painting. Compared with organic solvent-based inks, water-based inks are more environmentally friendly, and thus much more attractive for practical applications.

In this study, we report our exploitation on the fabrication of a porous cathode layer by inkjet printing using environmentally friendly water-based ink. A $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) + $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) composite cathode was used. For the easy sintering of the thin film layer prepared by inkjet printing because of the ultrafine powder size, the use of a pore former was also attempted. We demonstrated that both the pore former and powder loading in the ink are important to the microstructure and, consequently, the performance of the electrode. After optimization, the as-prepared composite electrode delivered comparable performance to that achieved by spray deposition, which is highly promising for its practical application in SOFCs.

## 2. Experimental

### 2.1. Cathode powder synthesis

The SSC powder was synthesized by a combined EDTA-citrate sol–gel method, while the SDC powder was synthesized using a hydrothermal process. All the related raw materials mentioned below were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China in analytical grade. For SSC, a stoichiometric amount of $Sm(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, and $Co(NO_3)_2 \cdot 6H_2O$ were mixed with the molar ratio of 0.5:0.5:1 and dissolved in deionized water. The complexing agents, EDTA and citric acid, were added in sequence according to the mole ratio of EDTA to metal ions to citric acid, i.e., 1:1:2. The pH value of the solution was adjusted to ~6 by adding an appropriate amount of ammonia. The red-brown gel, obtained after heating of the solution under stirring for several hours over a hot plate, was fired at 250 °C and then calcined at 1000 °C for 5 h in air to obtain the final product. For the preparation of SDC, a stoichiometric amount of $Sm(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in deionized water under stirring. Ammonia was used to adjust the pH value to ~10. The brown suspension was transferred into an autoclave and then placed in an oven at 180 °C for 24 h. After being cooled to room temperature, the obtained precipitate was collected via suction filtration and washed with water 3 times and then dried. The precipitation was subsequently fired at 800 °C for 5 h in air to obtain the SDC powder.

### 2.2. Cathode ink preparation

The as-synthesized SSC and SDC powders were used for the preparation of the water-based cathode ink. The SSC and SDC powders were mixed at a weight ratio of 70:30 and dispersed in water. Then appropriate amounts of polyethylene glycol 4000 (PEG-4000) as a pore former and glycerine and polyacrylic acid as additives was added into the suspension. The detailed compositions are given in Table 1. After being milled at 400 rpm for 1 h in a high-energy ball miller (Model Pulverisette 6, Fritsch) and then treated for 30 min with an ultrasonic probe (Model JY92-11DN, Scientz Biotechnology), a well-dispersed cathode ink was finally obtained. To explore the effect of the pore former on the printed cathode layer, two inks with different contents of PVB were prepared.

### 2.3. Cell fabrication

An anode-supported thin film electrolyte cell configuration was adopted. The anode substrates were prepared using a tape-cast method. First, the anode slurry of NiO(Chengdu ShuduNano-Science Co. Ltd.) and YSZ (8 mol%, Tosoh) at a weight ratio of 6:4 with dimethylbenzene (Sinopharm Chemical Reagent Co. Ltd.) and ethanol as solvents and fish oil (Sigma–Aldrich) as a dispersant was ball milled for 24 h. Second, some organic additives and PVB binder were added to the slurry, followed by another ball milling for 24 h to obtain the final slurry. Then the slurry was casted on the tape at a speed of 5 m $min^{-1}$ and dried in air for 12 h. Disk-shaped pellets were punched and sintered at 1100 °C for 2 h to obtain the anode substrates. Next, a thin-film YSZ electrolyte layer and SDC buffering layer in sequence were deposited onto one surface of the anode substrate via a wet powder spraying technique. The prepared half-cells were then co-fired at 1400 °C for 2 h in air to obtain the inkjet printing triple-layered substrate.

In the study, a modified HP Deskjet 2668 printer and black ink cartridge (HP CC640ZZ 818) were used as the printing unit and the ink container, respectively, with a printing resolution of 600 dpi. The inks were filled into cartridges using syringes. The printing speed was kept constant for the whole printing process. Typically, 20 s was required to produce a total surface area of 100 $cm^2$ for each printing. A total of 45 passes of the cathode were printed over the triple-layered substrate in a similar manner.

**Table 1**
Ink formulations used for inkjet printing.

| Constituent | SSC/SDC | $H_2O$ | PEG-4000 | PAA | Glycerine |
|---|---|---|---|---|---|
| Quantity (g) | 2 | 36.2 | 1 | 0.3 | 0.5 |