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Inkjet-printed Porous Silver Thin Film as a Cathode for Low-Temperature Solid Oxide Fuel Cell

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KEYWORDS: Inkjet printing; Sputtering; Silver thin film cathode; Low-temperature solid oxide fuel cell (LT-SOFC); electrochemical impedance spectroscopy (EIS).

ABSTRACT

This work reports the porous silver thin film cathode that was fabricated by a simple inkjet printing process for low-temperature solid oxide fuel cell applications. The electrochemical performance of inkjet-printed silver cathode was studied at 300 – 450 °C and was compared with silver cathodes that were fabricated by the typical sputtering method. Inkjet-printed silver cathodes showed lower electrochemical impedance due to its porous structure that facilitated the oxygen gaseous diffusion and oxygen surface adsorption-dissociation reactions. Typical sputtered nanoporous silver cathode became essentially dense after the operation and showed high impedance due to lack of oxygen supply. The results of long-term fuel cell operation show that the cell with an inkjet-printed cathode had a more stable current output for more than 45 hours at 400 °C. A porous silver cathode is required for high fuel cell performance, and the simple inkjet printing technique offers an alternative way of fabrication for such desirable porous structure with required thermal morphological stability.

INTRODUCTION

The wide application of solid oxide fuel cells (SOFCs) has been limited by the requirement of high operating temperatures, typically above 800 °C. Therefore, to lower the operating temperature without sacrificing the device's performance is one of the major trends to pursue. Recent efforts have shown impressive electrochemical performances of SOFCs below 500 °C by using nanoscale thin film electrolytes (often referred as μ -SOFCs) ¹ that minimize the ohmic resistance, and the obtained peak power densities were up to 1.3 W·cm⁻² at 450 °C ²⁻³. At such low temperatures, the oxygen reduction reaction (ORR) at the cathode becomes the most rate-limiting step that accounts for the majority of losses due to the sluggish cathode reaction kinetics

⁴⁻⁵. The impressive cell performances reported to date were mostly achieved by utilizing platinum (Pt), which is catalytically the most active material, as the cathode material. However, Pt, as one of the rare elements in the earth crust, is prohibitively expensive to be used for wide application. Therefore, finding substitutes for Pt is one of the most critical issues in order for SOFCs to be used in real-world applications at temperatures below 500 °C. In this regard, silver (Ag) can be a feasible candidate as the cathode for μ -SOFCs since it has good catalytic activity, excellent oxygen solubility ($\sim 10^{-6}$ mol $\cdot$ cm $^{-3}$ ⁶), and permeability (oxygen diffusivity $D=4.98 \times 10^{-3} \exp[(0.50\pm 0.13 \text{ eV}) k_B^{-1} T^{-1}]$ ⁶⁻⁷), which are critical properties for effective cathodic ORR. The superior electrical conductivity of Ag over conventional oxide cathode materials for SOFCs also minimizes the ohmic resistance. Some studies have shown that the cathode reaction kinetics of Ag on yttria-stabilized zirconia (YSZ) were comparable to or even better than that of noble metals like Pt due to the increased oxygen incorporation into the electrolyte ⁸⁻¹⁰. Besides, the lower cost of Ag is also attractive when compared to other noble metals.

The main issue of using pure Ag as the cathode material for SOFCs is its poor thermal-morphological stability. Ag is highly mobile at the elevated temperatures due to its relatively low melting point (961 °C) and high volatility (2 μ m thick Ag will be lost per year at 800 °C) ¹¹. Therefore, Ag was seldom used in pure metallic form at the temperature above 500 °C, and rather it was presented as a constitute of the composite with perovskites or ion-conducting electrolytes ¹²⁻²⁰. However, with the low operating temperature of μ -SOFCs, the technical feasibility of using Ag as a cathode is reconsidered.

For the ORR on Ag cathode, two possible pathways of oxygen diffusion were proposed ^{6, 21-22}. The first is through the bulk path as shown in Figure 1 (the path I), where the adsorbed oxygen molecules are dissociated into atomic oxygen and diffuse through the bulk Ag, and finally

reduced at the two-phase boundary (2PB), which is the two-dimensional interface between the Ag cathode and the electrolyte. The second route is through the surface path (the path II in Figure 1), where the adsorbed and dissociated oxygen molecules on Ag surface diffuse along the Ag surface and reduce at the triple phase boundary (TPB), which is the one-dimensional line interface where gaseous oxygen, Ag cathode, and electrolyte are in physical contact. The bulk path is expected to be the rate-limiting step at temperatures from 400 °C to 900 °C according to previous experimental results ^{6, 22-24}. Therefore, it is intuitive that the porous Ag cathode can facilitate ORR and results in a better fuel cell performance. Typical porous Ag electrode can be fabricated by applying the commercial Ag paste followed by a high-temperature (~800 °C) firing to build adhesion with the substrate. However, such high-temperature firing may cause mechanical failures of μ -SOFCs on the electrolyte layer. Also, the thickness and the pore size of the film made by Ag paste is typically tens of micrometers, which may not be suitable for the μ -SOFCs application.

Currently, sputtering is one of the most widely used methods for fabricating porous metal thin film electrodes such as Pt, Ag, Au, Ru, etc. ^{1-3, 25-28}, and by controlling the supplied gas pressure during the sputtering process, electrodes with nanoscale pores can be fabricated ²⁹. However, it is difficult to fabricate a porous Ag electrode, which is stable at the elevated temperature, by sputtering due to the relatively low melting point of Ag (961 °C) compare to Pt (1768 °C). According to the microstructure zone model of evaporation and sputtering ²⁹⁻³⁰, the resulting microstructure of thin films by sputtering will be affected by the ratio between the sputtering temperature (T) and the melting point of the material (T_m), T/T_m (in Kelvin). The higher ratio of T/T_m of silver will easily result in a denser structure during sputtering.

To utilize the good properties of Ag in the application as an SOFC cathode material, it is imperative to improve the thermal stability of Ag thin film cathodes. Shim *et al.* applied the nanosphere lithography technique to fabricate an Ag thin film nano-mesh having perforated pores inside the film with diameters around 500 - 600 nm¹⁰. The Ag nano-mesh remained stable for 2 hours without significant cell performance degradation, but the test was done at a very low operating temperature of 277 °C, which may not be sufficient to provide a satisfactory SOFC performance. Another recent work has demonstrated a temporarily improved thermal stability of sputtered porous Ag thin film cathode at 450 °C by introducing a 5 nm-thick of conformal capping layer of YSZ by the atomic layer deposition²⁰.

In addition to fabricating Ag thin film with a porous structure and maintaining the porosity at elevated temperatures, the electrical connectivity of the Ag cathode is also an important parameter to consider for the current collection. If the Ag thin film deposited on the electrolyte is not sufficiently thick, the thermally driven agglomeration will cause breakage in the thin film network that resulted in electrical disconnection³¹. Simrick *et al.* reported that at least 1 µm of thickness is required for thin film Ag cathode on a zirconia substrate to prevent the network breakage at temperatures below 500 °C³¹.

In this work, the inkjet-printed silver thin film that fulfilled the requirement of porous structure and thermal-morphological stability was demonstrated to overcome the difficulty of fabricating a porous silver cathode by conventional sputtering techniques. Inkjet printing technique could fabricate dense Ag films on ceramic oxide substrates³² as well as mesoporous Ag films³³. A porous Ag cathode with connected pores throughout the film with the thickness larger than 1 µm was demonstrated for the application in low-temperature SOFCs. The electrochemical

impedance spectroscopy (EIS) and polarization (I-V) curves of inkjet-printed Ag cathodes were compared with those of sputtered Ag and sputtered Pt cathodes.

EXPERIMENTAL METHODS

Fabrication of Silver Thin Film Cathodes

The porous Ag cathodes were fabricated by MicroFab JetLab4 printing system (MicroFab Technologies Inc., USA). The outlet diameter of the printing piezoelectric nozzle is 50 μm . The ink for Ag deposition was prepared by adding 10 wt. % Ag nanoparticles with 200 nm in diameter into a humectant solution (30 % ethylene glycol and 70 % water). Details of Ag nanoparticle synthesis can be found in the reference ³⁴. 100 μm -thick single crystalline YSZ <100> wafers (8YSZ, Latech Scientific Supply Pte. Ltd., Singapore) were used as the electrolyte substrate for Ag cathode printing, and the YSZ substrate was heated to 50 $^{\circ}\text{C}$ during the deposition. Droplets with 56 μm in mean diameter were ejected at a speed of 1.65 $\text{m}\cdot\text{s}^{-1}$ at 250 Hz. The spacing between each ejected droplet was 80 μm and the distance between two printed lines was 20 μm . The cathode was printed in a circular shape with the diameter of 6 mm. A total of 6 printed layers was required to complete a fully connected Ag film with a thickness of approximately 2.5 μm . The as-printed Ag films were baked at 200 $^{\circ}\text{C}$ for 30 min to remove the solvent in the ink and to establish connectivity between the Ag nanoparticles for required electrical conductivity. Finally, the Ag thin films were annealed at 300 $^{\circ}\text{C}$ for 1 hour to create the interconnected pores. For comparison, the conventional sputtered Ag cathode thin films were also prepared with the thickness of 1 and 2.5 μm . The deposition was carried out by a custom-built radio-frequency (RF) sputtering apparatus at 6 mTorr of Ar pressure and 100 W of RF power at room temperature (23 $^{\circ}\text{C}$), with a resulting deposition rate of 35 $\text{nm}\cdot\text{min}^{-1}$. Both the

inkjet-printed and RF sputtered Ag thin films were annealed at 250 °C, 300 °C, 350 °C, and 400 °C for 1 hour in a tube furnace to examine the morphological evolution at our targeted operating temperature range. The surface and cross-sectional morphology of the Ag cathodes were examined before and after cell test using a field emission secondary electron microscope (FESEM, JEOL JSM-7600F, USA).

Fuel Cell Fabrication

Fuel cells with either inkjet-printed or RF sputtered Ag cathodes were fabricated to characterize the cathode impedance and the fuel cell performance. A nanoporous Pt thin film with the thickness of 100 nm was sputtered on the other side of the YSZ substrate as the anode for all cells tested, the deposition parameters can be found in the previous reports^{28, 35}. A fuel cell with a typical nanoporous Pt cathode was also fabricated as a reference to compare the cathode performance with Ag cathodes, and it was deposited with the same parameters as the porous Pt anode. The diameter of all the cathodes deposited on the YSZ was 6 mm, and the lateral dimension of the cathode is the active area of all cells. The schematics and image of the fabricated SOFCs are illustrated in Figure 2.

Electrochemical Characterization

The polarization resistance and the current density-voltage curves of the SOFCs using the 300 °C-annealed thin film cathodes were measured at 300 °C to 400 °C using a potentiostat (Solartron 1470E, Solartron Analytical, USA) with a frequency analyzer (Solartron 1255B, Solartron Analytical, USA). The characterization was done using pure hydrogen (99.99%) as a fuel at a flow rate of 20 sccm and ambient air as an oxidant. The EIS measurement was conducted at the frequency range from 1 MHz to 0.1 Hz with the oscillation amplitude of 50 mV. The impedance data was fitted by Z-Plot software (Scribner Associates Inc., USA) based on

complex nonlinear least-squares fitting method, using the model of one resistor with two parallel resistors/constant phase elements (CPE) in series. The polarization impedance was normalized by the cell active area to get the area specific resistances (ASR) of the fuel cells.

RESULTS AND DISCUSSION

Microstructures of Silver Cathode Thin Films

Figure 3 shows the comparison of cross-sectional microstructures of Ag thin films prepared by inkjet printing and by RF sputtering. After the low-temperature baking at 200 °C to remove the solvent, the inkjet-printed Ag nanoparticles were sintered to form a continuous film (Figure 3a). More obvious agglomeration of Ag particles on the surface of the film was observed after it was annealed at 250 °C (Figure 3b) due to the inhomogeneous nucleation that made it energetically more favorable for agglomeration³⁶. The surface agglomeration continued up to the annealing temperature of 300 °C, where an obvious change in pore size inside the film was observed (Figure 3c). As the annealing temperature increased to 350 °C and 400 °C, the pore sizes did not show any noticeable change (Figure 3d and Figure 3e). Therefore, before the fuel cell test, the inkjet-printed Ag cathode was pre-annealed at 300 °C to drive its microstructure change to a porous structure with interconnected pores, this would also help to prevent severe morphological change during the test and affect the measurement. Note that the difference among the thickness of the inkjet-printed films was due to non-uniform ink distribution during the printing process. On the other hand, the sputtered Ag films appeared to be mostly dense with little pores exist over all annealing temperatures (Figure 3g – Figure 3j).

EIS Analysis on Silver Cathodes

Oxygen reduction reaction at the cathode is known to be the rate-limiting step for the entire fuel cell reactions during low-temperature operation. To investigate how the different cathode structures affect the ORR process, the cathode impedance measurements were performed. Figure 4 shows the Nyquist plots measured on the cells using inkjet-printed Ag (300 °C annealed), sputtered Ag (1 μm or 2.5 μm), and sputtered porous Pt cathode at 400 °C. Two distinguishable arcs in the plots for the cells with Ag cathode were observed (Figure 4a – Figure 4c). The high-frequency arcs were ascribed to the ohmic resistance with a capacitance value less than 10^{-9} F, which was mainly associated with the series ionic resistance of electrolyte and electronic resistance in the electrode as well as the contact resistance³⁶, and they were independent of the voltage. The low-frequency arcs were attributed to the electrochemical reaction processes on the electrode. In this case, it can be attributed mainly to the cathode ORR polarization process³⁶⁻³⁷. For the Pt cathode, only one lower frequency arc was observed in the Nyquist plot (Figure 4d), and it was mainly attributed to cathode ORR process. The ASR of the cathode can be calculated from the EIS results, the equivalent circuit model, which consists of one resistor and two parallel resistor-constant phase elements (R-CPE) in series, was used in the EIS fitting. The equivalent circuit used for fitting and the fitting results can be found in the Electronic Supplementary Information.

For the electrode ASR analysis, we assumed that anodic impedance is negligible since ORR processes at the cathode are more sluggish than hydrogen oxidation process³⁸. Also, identical Pt anode was applied on all samples. Therefore, the main differences of electrode ASR were originated from cathodes with different microstructures. Figure 5 shows the calculated electrode ASR by EIS fitting and it is clearly shown that the dense Ag cathode had higher ASR, and the ASR increased with the cathode thickness. The Pt cathode had lowest ASR among all samples

due to its nanoporous structure, which effectively increases the reaction site for ORR. However, such nanoporous Pt structure is not stable at the elevated temperature since it may suffer from severe degradation in few hours of operation as the earlier studies reported^{28, 35}.

The values of polarization ASR observed are generally in the sequence of Pt < inkjet-printed Ag < sputtered Ag (1 μm) < sputtered Ag (2.5 μm), as shown in Figure 5. These results indicate that the bulk oxygen diffusion is the rate-determining step for dense Ag cathode and the fuel cell performance aggravates as the Ag thickness increases. The use of porous Ag facilitates ORR process by reducing the ASR. Interestingly, higher electrode ASR of dense Ag cathode was observed at 0.5 V and 0.3 V (Figure 5b and Figure 5c). This phenomenon is not usual in SOFCs and rather similar in polymer exchange membrane fuel cells, which is thought to be increased in mass transfer limitation³⁹.

From the cathode ASR extracted from EIS results measured at 300 to 450 °C, the activation energy of Ag and Pt cathodes were calculated. Table 1 summarized the activation energy (E_a) of Ag and Pt cathodes under different voltages. The activation energy of 1 μm -thick sputtered Ag cathode was ~1.2 eV within the measured voltage range while the activation energy of inkjet-printed Ag cathode was lower than 1.1 eV and decreased with increasing voltages. These results indicate that the change of electrochemical reaction process under different voltages. The activation energy of inkjet-printed Ag was close to the activation energy of oxygen adsorption and dissociation process, 1 eV, experimentally reported by Van Herle *et al.*⁶ and 0.6 – 1.3 eV from the calculation of density functional theory by Wang *et al.*⁴⁰. Therefore, the oxygen adsorption and dissociation could be the dominant processes for porous Ag cathode at the reduced temperature. For the Pt cathode, since Pt has a higher oxygen reduction activity and a

lower oxygen binding energy compared to Ag³⁸, its activation energies for cathode reactions were generally lower than that of Ag.

Fuel Cell Performance

Figure 6 (a) – Figure 6 (c) shows the polarization (I - V) curves of SOFCs with inkjet-printed Ag, sputtered Ag, and sputtered Pt cathodes. The cell with inkjet-printed porous Ag cathode had higher peak power density than those of cells with sputtered dense Ag cathodes. At 400 °C, the peak power density of the cell with inkjet-printed Ag, sputtered Ag (1 μm), sputtered Ag (2.5 μm), and Pt cathode was 0.58, 0.37, 0.12, and 0.75 mW·cm⁻², respectively. These results were in line with EIS results, the lower ASR resulted in higher cell output. The nanoporous Pt structure provided a high density of reaction site (i.e. TPB), which is essential to improve the cell performance. While the sputtered Ag could not retain its nanoporous structure and became essentially dense at the operating temperature, a significant mass transport loss on the cell with 2.5 μm-thick sputtered Ag was observed at all temperatures because of insufficient supply of oxygen at the Ag|YSZ interface and such loss was reduced when the thickness of cathode decreased to 1 μm. Unlike sputtered Ag cathodes, the inkjet-printed Ag cathode could retain porous structure at the operating temperature and resulted in higher power density. However, the inkjet-printed Ag could not provide such a high TPB density as sputtered Pt, the power density is therefore slightly lower for the cells with the inkjet-printed Ag cathode.

Considering the long-term operating stability of Ag cathodes, Figure 6(d) shows the current output test of the fuel cell with inkjet-printed porous Ag at 400 °C for over 45 hours. The fluctuation of output current was observed during the test, which may come from the slight change of Ag cathode morphology during the test that caused the change of effective ORR site. After the test, the current density was about 12 % lower than the initial current density. The

current density of sputtered nanoporous Ag cathode decreased more than 68% after 20 hours of operation. An earlier study also showed that when nanoporous Pt cathode was used, the current output decreased more than 86 % after operating at 450 °C for 40 hours ³⁵. The results suggest that pure nanoporous metal cathode may not be suitable for long-term operation.

The comparison of Ag thin film morphology before and after fuel cell test is shown in Figure 7. The inkjet-printed Ag film still remained a porous structure with larger pore size after cell test, while the sputtered Ag films (1 µm and 2.5 µm) became denser with larger grain size. These results were similar to the samples which were annealed at 400 °C as shown in Figure 3.

To facilitate oxygen gas diffusion on the cathode, a porous structure is necessary. Therefore, from Figure 3 and Figure 7, sputtering technique, which is typically used to create a porous thin film electrode structure, may not be suitable as a deposition method for porous Ag thin film, compared to the inkjet-printed technique.

CONCLUSIONS

The Ag cathodes fabricated by two methods, inkjet-printing and sputtering, were examined at 300 °C to 450 °C using EIS technique. The inkjet-printed Ag film maintained a porous structure at the elevated temperature and stable current output test at 400 °C for 45 hours. By introducing a porous structure within Ag thin film cathode, the polarization resistance was significantly reduced at temperatures below 400 °C. For cathode thin film fabrication, inkjet printing technique using Ag nanoparticles can be an excellent method to create morphologically stable and porous Ag electrodes, which is difficult to be obtained by conventional vacuum-based deposition methods.

FIGURES

Figure 1. Schematic of possible oxygen diffusion pathways of Ag on YSZ electrolyte.

Figure 2. Schematics of SOFCs with (a) inkjet-printed porous Ag cathode with thickness of 2.5 μm ; (b) sputtered nanoporous Ag cathode with two thicknesses of 1 μm or 2.5 μm ; (c) sputtered nanoporous Pt cathode; and (d) image of the SOFC with a 6 mm circular inkjet-printed Ag cathode on the transparent YSZ electrolyte substrate. The 100 nm-thick of porous Pt anode (the dark gray square) on the other side of the YSZ substrate.

Figure 3. Cross-sectional views of the microstructure evolution of Ag thin films annealed at 250 °C to 400 °C on YSZ substrate for (a) – (e): inkjet-printed Ag, and (f) – (j): RF sputtered Ag. The inkjet-printed Ag thin film annealed at 300 °C and the as-sputtered Ag thin film was used as the cathode for subsequent tests.

Figure 4. Electrochemical impedance spectrum of (a) inkjet-printed porous Ag cathode, (b) 1 μm -thick sputtered Ag cathode, (c) 2.5 μm -thick sputtered Ag cathode, and (d) 100 nm-thick sputtered Pt cathode with equivalent circuit fitting results. All results were measured at 400 °C and 0.3 V.

Figure 5. Polarization ASR plots derived from EIS fitting at 300 – 450 °C and at the voltage of (a) OCV, (b) 0.5 V, and (c) 0.3 V.

Figure 6. Polarization (I-V) curves of SOFCs measured at (a) 300 °C, (b) 350 °C, and (c) 400 °C. (d) Current density over 45 hours at 400 °C for the SOFC with inkjet-printed Ag and sputtered Ag cathode. The output current decreased 12.1 % and 68.1 % on average at 0.7 V after the test for inkjet-printed Ag and sputtered Ag, respectively.

Figure 7. (a) – (c) Morphology of as-prepared Ag thin films before fuel cell test. (d) – (f) Morphologies of Ag thin film after fuel cell test at 400 °C.

TABLES

Table 1. Activation energies of Ag and Pt cathodes calculated from polarization ASR fitting results.

	E _a (eV)		
	OCV	0.5 V	0.3 V
Sputtered Ag (1μm)	1.22±0.03	1.20±0.02	1.22±0.03
Sputtered Ag (2.5μm)	1.20±0.14	0.45±0.08	0.50±0.08
Inkjet-printed Ag	1.10±0.06	0.96±0.06	0.82±0.09
Pt	0.50±0.07	0.73±0.04	0.80±0.02

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Detailed electrochemical impedance spectroscopy fitting results.

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ABBREVIATIONS

EIS, electrochemical impedance spectroscopy; YSZ, yttria-stabilized zirconia; TPB, triple phase boundary; 2PB, two-phase boundary; ORR, oxygen reduction reaction; SOFCs, solid oxide fuel cells; PVD, physical vapor deposition; CPE, constant phase element; ASR, area specific resistance;

REFERENCES

- (1) Evans, A.; Bieberle-Hütter, A.; Rupp, J. L. M.; Gauckler, L. J. Review on Microfabricated Micro-Solid Oxide Fuel Cell Membranes. *J. Power Sources* **2009**, *194*, 119-129.
- (2) An, J.; Kim, Y. B.; Park, J.; Gur, T. M.; Prinz, F. B. Three-Dimensional Nanostructured Bilayer Solid Oxide Fuel Cell with 1.3 W/cm² at 450 degrees C. *Nano Lett.* **2013**, *13*, 4551-4555.
- (3) Chao, C. C.; Hsu, C. M.; Cui, Y.; Prinz, F. B. Improved Solid Oxide Fuel Cell Performance with Nanostructured Electrolytes. *ACS Nano* **2011**, *5*, 5692-5696.
- (4) Adler, S. B. Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes. *Chem. Rev.* **2004**, *104*, 4791-4843.

- (5) Wachsman, E. D.; Lee, K. T. Lowering the Temperature of Solid Oxide Fuel Cells. *Science* **2011**, *334*, 935-939.
- (6) Vanherle, J.; McEvoy, A. J. Oxygen Diffusion Through Silver Cathodes for Solid Oxide Fuel Cells. *J. Phys. Chem. Solids* **1994**, *55*, 339-347.
- (7) Kontoulis, I.; Steele, B. C. H. Determination of Oxygen Diffusion in Solid Ag by an Electrochemical Technique. *Solid State Ionics* **1991**, *47*, 317-324.
- (8) Baker, R.; Guindet, J.; Kleitz, M. Classification Criteria for Solid Oxide Fuel Cell Electrode Materials. *J. Electrochem. Soc.* **1997**, *144*, 2427-2432.
- (9) Vladikova, D. E.; Stoyanov, Z. B.; Barbucci, A.; Viviani, M.; Carpanese, P.; Kilner, J. A.; Skinner, S. J.; Rudkin, R. Impedance Studies of Cathode/Electrolyte Behaviour in SOFC. *Electrochim. Acta* **2008**, *53*, 7491-7499.
- (10) Shim, J. H.; Kim, Y. B.; Park, J. S.; An, J.; Gur, T. M.; Prinz, F. B. Patterned Silver Nanomesh Cathode for Low-Temperature Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **2012**, *159*, B541-B545.
- (11) Barnett, S. A. A New Solid Oxide Fuel-Cell Design Based on Thin-Film Electrolytes. *Energy* **1990**, *15*, 1-9.
- (12) Wang, L. S.; Barnett, S. A. Deposition, Structure, and Properties of Cermet Thin-Films Composed of Ag and Y-Stabilized Zirconia. *J. Electrochem. Soc.* **1992**, *139*, 1134-1140.
- (13) Wang, S. R.; Kato, T.; Nagata, S.; Honda, T.; Kaneko, T.; Iwashita, N.; Dokiya, M. Performance of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}}\text{-Ag}$ Cathode for Ceria Electrolyte SOFCs. *Solid State Ionics* **2002**, *146*, 203-210.

- (14) Haanappel, V. A. C.; Rutenbeck, D.; Mai, A.; Uhlenbruck, S.; Sebold, D.; Wesemeyer, H.; Rowekamp, B.; Tropsch, C.; Tietz, F. The Influence of Noble-Metal-Containing Cathodes on The Electrochemical Performance of Anode-Supported SOFCs. *J. Power Sources* **2004**, *130*, 119-128.
- (15) Sholklapper, T. Z.; Radmilovic, V.; Jacobson, C. P.; Visco, S. J.; De Jonghe, L. C. Nanocomposite Ag-LSM Solid Oxide Fuel Cell Electrodes. *J. Power Sources* **2008**, *175*, 206-210.
- (16) Zhou, W.; Ran, R.; Shao, Z. P.; Cai, R.; Jin, W. Q.; Xu, N. P.; Ahn, J. Electrochemical Performance of Silver-Modified Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} Cathodes Prepared via Electroless Deposition. *Electrochim. Acta* **2008**, *53*, 4370-4380.
- (17) Li, Q. A.; Sun, L. P.; Huo, L. H.; Zhao, H.; Grenier, J. C. Electrochemical Performance of La₁₋₆Sr_{0.4}Ni_{0.4}-Ag Composite Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells. *J. Power Sources* **2011**, *196*, 1712-1716.
- (18) Fan, L. D.; Chen, M. M.; Wang, C. Y.; Zhu, B. Pr₂NiO₄-Ag Composite Cathode for Low Temperature Solid Oxide Fuel Cells with Ceria-Carbonate Composite Electrolyte. *Int. J. Hydrogen Energy* **2012**, *37*, 19388-19394.
- (19) Wang, L. S.; Barnett, S. A. Ag-Perovskite Cermets for Thin-Film Solid Oxide Fuel-Cell Air-Electrode Applications. *Solid State Ionics* **1995**, *76*, 103-113.
- (20) Li, Y. K.; Choi, H. J.; Kim, H. K.; Chean, N. K.; Kim, M.; Koo, J.; Jeong, H. J.; Jang, D. Y.; Shim, J. H. Nanoporous Silver Cathodes Surface-Treated by Atomic Layer Deposition of

Y:ZrO₂ for High-Performance Low-Temperature Solid Oxide Fuel Cells. *J. Power Sources* **2015**, *295*, 175-181.

(21) Kenjo, T.; Takiyama, H. Oxygen Permeation in Ag/Ysz Air Cathodes. *Electrochim. Acta* **1994**, *39*, 2685-2692.

(22) Jimenez, R.; Kloidt, T.; Kleitz, M. Reaction-Zone Expansions and Mechanism of The O-2, Ag/Yttria-Stabilized Zirconia Electrode Reaction. *J. Electrochem. Soc.* **1997**, *144*, 582-585.

(23) Moghadam, F. K.; Stevenson, D. A. Oxygen Diffusion and Solubility Studies in Ag and Pt Using Ac Impedance Spectroscopy. *J. Electrochem. Soc.* **1986**, *133*, 1329-1332.

(24) Vanherle, J.; Mcevoy, A. J.; Thampi, K. R. Oxygen Reduction at Porous and Dense Cathodes for Solid Oxide Fuel-Cells. *Electrochim. Acta* **1994**, *39*, 1675-1680.

(25) Su, P. C.; Chao, C. C.; Shim, J. H.; Fasching, R.; Prinz, F. B. Solid Oxide Fuel Cell with Corrugated Thin Film Electrolyte. *Nano Lett.* **2008**, *8*, 2289-2292.

(26) Tsuchiya, M.; Lai, B. K.; Ramanathan, S. Scalable Nanostructured Membranes for Solid-Oxide Fuel Cells. *Nat Nanotechnol* **2011**, *6*, 282-286.

(27) Su, P. C.; Prinz, F. B. Nanoscale Membrane Electrolyte Array for Solid Oxide Fuel Cells. *Electrochem. Commun.* **2012**, *16*, 77-79.

(28) Yu, C.-C.; Kim, S.; Baek, J. D.; Li, Y.; Su, P.-C.; Kim, T.-S. Direct Observation of Nanoscale Pt Electrode Agglomeration at the Triple Phase Boundary. *ACS Appl. Mater. Interfaces* **2015**, *7*, 6036-6040.

- (29) Thornton, J. A. Influence of Apparatus Geometry and Deposition Conditions on Structure and Topography of Thick Sputtered Coatings. *J Vac Sci Technol* **1974**, *11*, 666-670.
- (30) Thornton, J. A. High-Rate Thick-Film Growth. *Annu. Rev. Mater. Sci.* **1977**, *7*, 239-260.
- (31) Simrick, N. J.; Kilner, J. A.; Atkinson, A. Thermal Stability of Silver Thin Films on Zirconia Substrates. *Thin Solid Films* **2012**, *520*, 2855-2867.
- (32) Camarchia, V.; Chiolerio, A.; Cotto, M.; Fang, J.; Ghione, G.; Pandolfi, P.; Pirola, M.; Quaglia, R.; Ramella, C. Demonstration of Inkjet-Printed Silver Nanoparticle Microstrip Lines on Alumina for RF Power Modules. *Org. Electron.* **2014**, *15*, 91-98.
- (33) Chiolerio, A.; Virga, A.; Pandolfi, P.; Martino, P.; Rivolo, P.; Geobaldo, F.; Giorgis, F. Direct Patterning of Silver Particles on Porous Silicon by Inkjet Printing of a Silver Salt via In-Situ Reduction. *Nanoscale Res Lett* **2012**, *7*, 1-7.
- (34) Lien, D. H.; Kao, Z. K.; Huang, T. H.; Liao, Y. C.; Lee, S. C.; He, J. H. All-Printed Paper Memory. *ACS Nano* **2014**, *8*, 7613-7619.
- (35) Liu, K.-Y.; Fan, L.; Yu, C.-C.; Su, P.-C. Thermal Stability and Performance Enhancement of Nano-Porous Platinum Cathode in Solid Oxide Fuel Cells By Nanoscale ZrO₂ Capping. *Electrochem. Commun.* **2015**, *56*, 65-69.
- (36) Holme, T. P.; Pornprasertsuk, R.; Prinz, F. B. Interpretation of Low Temperature Solid Oxide Fuel Cell Electrochemical Impedance Spectra. *J. Electrochem. Soc.* **2010**, *157*, B64.
- (37) Tuller, H. L.; Litzelman, S. J.; Jung, W. Micro-Ionics: Next Generation Power Sources. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3023-34.

(38) Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the Overpotential For Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004**, *108*, 17886-17892.

(39) Yuan, X. Z. R.; Song, C.; Wang, H.; Zhang, J. *Electrochemical Impedance Spectroscopy in PEM Fuel Cells: Fundamentals and Applications*. Springer London: **2009**.

(40) Wang, J. H.; Liu, M. L.; Lin, M. C. Oxygen Reduction Reactions in the SOFC Cathode of Ag/CeO₂. *Solid State Ionics* **2006**, *177*, 939-947.

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