Short communication

Silver-perovskite composite SOFC cathodes processed via mechanofusion

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Abstract

Atomized silver spheres ($\approx$20–50 μm diameter) were coated with 1 μm thick layers of $(La_{0.6}Sr_{0.4})_{0.98}Co_{0.2}Fe_{0.8}O_3$ or $Sm_{0.5}Sr_{0.5}CoO_3$ via a mechanofusion dry processing method. The materials were subsequently assessed as solid oxide fuel cell cathodes on anode-supported YSZ electrolytes at 650–750 °C. The materials were subject to significant electrochemical conditioning during initial cell operation, and factors, such as temperature and operating voltage, affecting the conditioning rate are discussed. Post-conditioned power densities (at 0.7 V) were typically 550–650, 400–450 and 300–350 mW cm^{-2} at 750, 700 and 650 °C, respectively. Though power degradation rates of $\approx$7.5 and 4.5% (per 1000 h) were observed at 750 and 700 °C, respectively, no degradation was detected over almost 2000 h of testing at 650 °C.
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1. Introduction

A previous study by the authors [1] highlighted a novel solid oxide fuel cell (SOFC) cathode composite composed of silver spherical cores ($\approx$10–50 μm diameter) coated with a 1 μm layer of $(La_{0.6}Sr_{0.4})_{0.98}Fe_{0.8}Co_{0.2}O_3$ (LSCF-6428) powder. The composite was formed via a dry coating technique known as "mechanofusion." In the mechanofusion process, a powder mixture is subjected to various mechanical forces as it passes through a variable gap ($\approx$3 mm for this study) in a rotating device (Fig. 1a). As a result, small guest particles can be coated and bonded onto the surfaces of larger host particles without using binder of any kind (Fig. 1b). The degree of coverage is dependent on the particle size ratio of the host to guest powders (typically a host:guest ratio of >10:1 is required), the proportion of the guest material, the relative adhesive properties of the host and guest particles, and the energy input from the machine. An excellent review of mechanofusion and similar dry coating techniques is presented by Pfeffer et al. [2].

Preliminary data from the previous study [1] indicated that the performance of composite Ag-LSCF cathodes is characterized by initially low power (<100 mW cm^{-2} at 750 °C and 0.7 V) followed by substantial conditioning over a 50–100 h period to achieve power densities approaching 650 mW cm^{-2}. Phenomena responsible for the conditioning characteristics of these materials were not conclusively confirmed though it appeared that wetting (diffusion) of the coated spheres along the electrolyte surface likely played a role by increasing the electrical contact area between the cathode and the electrolyte, and additionally providing an enhanced triple phase boundary area. It also appeared that the role of the coating was to provide more controlled wetting of the silver since for uncoated silver spheres, excessive silver diffused across almost the entire electrolyte surface and resulted in air starvation of the cathode. No silver diffusion was observed for cells utilizing coated silver spheres held at open circuit voltage (OCV: zero current) and 750 °C for >250 h suggesting an electrochemically activated migration process. The term electromigration is used to describe mass transport of a conductor under an applied electric field, and such a phenomenon has previously been observed for silver by Ho and Huntington [3] at temperatures between 670 and 880 °C. Despite reasonable power densities at 750 °C, the Ag-LSCF composite was subject to ~10% power degradation per 1000 h (at 0.7 V) after a performance plateau around 200 h. However, for cells operated at 700 °C (exhibiting $\approx$450 mW cm^{-2} at 0.7 V)

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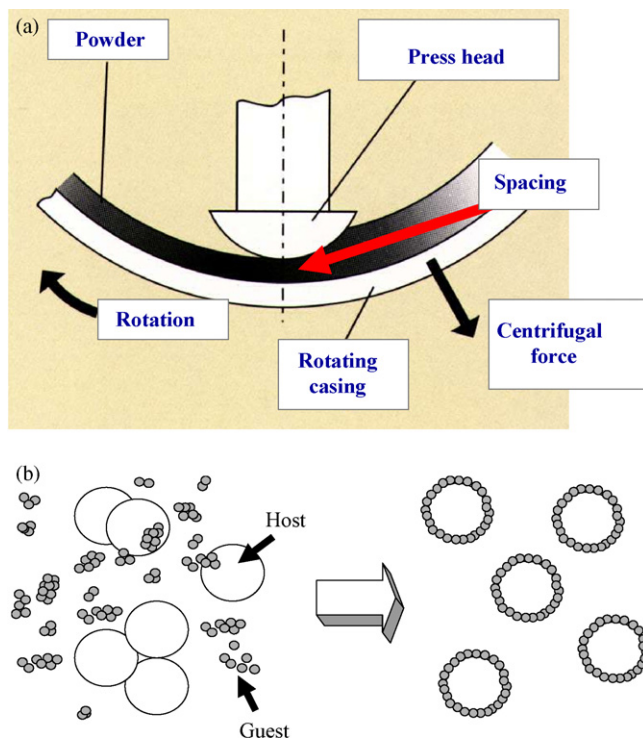
Fig. 1. (a and b) Principle of the mechanofusion process.

Fig. 2. Performance variability for similarly processed Ag-LSCF cells.

improved stability was observed, and the power degradation during a >2000 h test was ≈3% per 1000 h (at 0.7 V).

This investigation is a short continuation of the aforementioned study and details the role of materials and testing variables on the conditioning and long-term degradation of these composite cathodes. With respect to coatings $Sm_{0.5}Sr_{0.5}CoO_3$ (SSCo-5050) was considered in addition to the previously studied $(La_{0.6}Sr_{0.4})_{0.98}Co_{0.2}Fe_{0.8}O_3$ (LSCF-6428) since this composition is known to possess high oxygen ion conductivity and electro-catalytic activity towards oxygen reduction [4,5]. However, the coating composition was only considered with respect to long-term stability since supposedly "identical" coatings of LSCF on Ag had produced varied conditioning characteristics and post-conditioned power densities when tested at 750 °C and 0.7 V (Fig. 2), and any differences when using the SSCo coating were within this degree of variability. Regarding the influence of test variables on cell behavior temperature (700, 750, and 800 °C), and operating voltage (0.5 and 0.7 V) were analyzed.

2. Experimental

Anode-supported electrolyte (8YSZ) membranes (1 mm total thickness with ≈10 m thick YSZ membrane and 25 mm diameter) were produced via standard organic tape-casting and tape lamination procedures, co-sintered at 1375 °C for 1 h, and subsequently creep-flattened at 1200 °C for 2 h. $(La_{0.6}Sr_{0.4})_{0.98}Fe_{0.8}Co_{0.2}O_3$ and $Sm_{0.5}Sr_{0.5}CoO_3$ cathodes and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC-20) interlayer powders were supplied by Praxair Specialty Ceramics, Seattle, WA. Atomized silver spheres were purchased from Technic Inc. (Engineered Powders
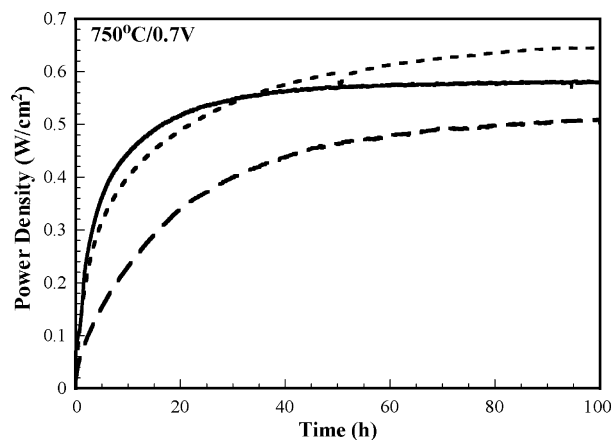
Division), Woonsocker, RI. The coated Ag composites (typically ≈5 wt.% oxide powder) were produced via a mechanofusion technique using a Hosokawa Mechanofusion System AMS-Mini. Processing and subsequent microstructural optimization, with respect to maximizing surface coverage, was performed by Hosokawa Micron Powder Systems, Summit, NJ, and is not the subject of this study. SDC-20 interlayers (≈5 μm sintered thickness) were applied to the anode-supported YSZ membranes via screen-printing, and sintered at 1200 °C for 2 h; the sintered SDC layers contained ≈25–35% porosity. Such layers are typically used to prevent interaction between the cathode and the YSZ electrolyte resulting in the formation of interfacial and resistive La- and or Sr-zirconate phases. Anode current collectors (Ni mesh embedded in NiO paste) were co-sintered with the ceria. Cathode compositions were applied by screen-printing (1.6 cm diameter print), and then sintered in situ during heat up (and sealing) of the cell to 800 °C. The cathode area (2 cm^2) was used as the active cell area to calculate power density and area specific resistance. A combination of gold mesh and foil were used as the cathode current collector, and simply pressed into the wet cathode ink prior to heat up. The cells were sealed to alumina test fixtures using Aremco cements (sintered at 800 °C/1 h), and compressive stress (≈10 psi) applied to the cell via a perforated alumina stub spring loaded outside the furnace hot zone (detailed in [6]). Current–voltage (I–V) data was recorded at 650–750 °C and 0.5–0.7 V for 250 to >2000 h using a Solartron 1480 Multistat. 48.5%H_2–48.5%N_2–3% H_2O was flowed to the anode at 200 sccm, and air to the cathode at 300 sccm.

3. Results and discussion

3.1. Effect of operating variables on cell conditioning

Two operating variables were considered with respect to the conditioning characteristics of the cells, namely (1) temperature (at constant voltage: 0.7 V) and (2) voltage (at constant temperature: 700 °C). All of the data presented pertains to Ag spheres coated with LSCF-6428 though almost identical trends were observed for the Ag-SSCo composite materials. Fig. 3 indicates
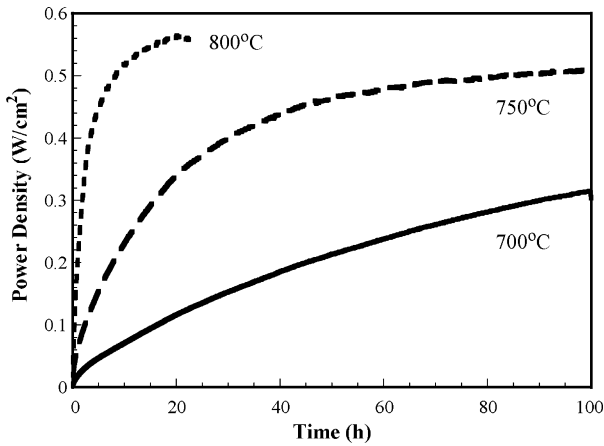
Fig. 3. Influence of operating temperature (700–800 °C) on Ag-LSCF conditioning at 0.7 V.

Fig. 5. Long-term performance of anode-supported SOFC utilizing Ag-SSCo composite cathode (750 °C/0.7 V).

a strong dependence on operating temperature. At 800 °C the cell conditioned in less than 20 h, at 750 °C much of the conditioning had taken place after 50 h of operation, whereas conditioning was still occurring after 100 h of operation at 700 °C. Calculated cell power density conditioning rates during the first 10 h of operation were 7, 22 and 50 mW cm^{-2} per hour at 700, 750 and 800 °C, respectively. Fig. 4 indicates an equally strong dependence of cell conditioning on operating voltage (and current density). At 0.7 V and 700 °C the power density conditioning rate is 7 mW cm^{-2} per hour compared to 43 mW cm^{-2} per hour at 0.5 V. These findings would appear to support the claim from our previous paper [1] that the conditioning mechanism is caused by the electromigration of Ag across the SDC interlayer surface. Indeed according to Ho and Huntington [3] the velocity of migrating ions increases with both temperature and current density.

3.2. Long-term behavior of Ag-SSCo composite

From the previous work [1] the power degradation rate of the Ag-LSCF composite was approximately 7% per 1000 h at 750° and 0.7 V, and 3–4% at 700 °C. From the previous

study the source of degradation at higher operating temperatures was attributed to continued (and excessive) diffusion of silver across the SDC interlayer resulting in decreased triple phase boundary area and a restriction of air access to the cathode-electrolyte interface. The rates of degradation with the SSCo coating at 750 and 700 °C are similar as depicted in Figs. 5 and 6, respectively. However, for this study the Ag-LSCF and Ag-SSCo compositions were also tested at 650 °C/0.7 V, shown in Figs. 7 and 8, respectively. Both specimens were initially conditioned at 750 °C/0.5 V for approximately 50 h. Subsequently, the Ag-LSCF composite was operated at 650 °C/0.7 V, and continued to condition for >600 h (achieving a power density of ≈400 mW cm^{-2}) after which it demonstrated stable performance for ≈1200 h. After the initial conditioning of the Ag-SSCo composite at 750 °C/0.5 V this specimen was operated at 750 °C/0.7 V until it started to show initial signs of degradation at ≈500 h at which point the operating temperature was dropped to 650 °C. Operating at 650 °C/0.7 V the Ag-SSCo composite indicated zero degradation over 1900 h and achieved a power density of ≈350 mW cm^{-2}.
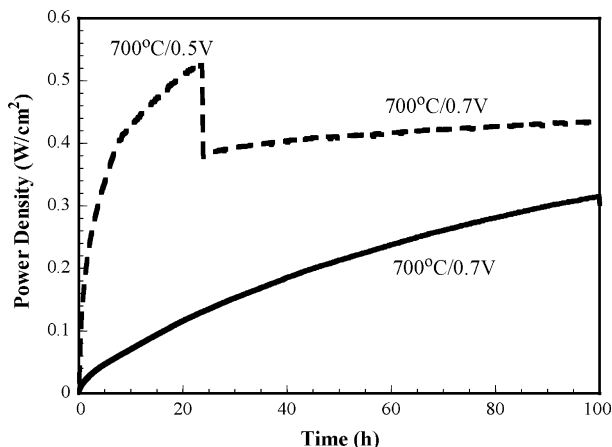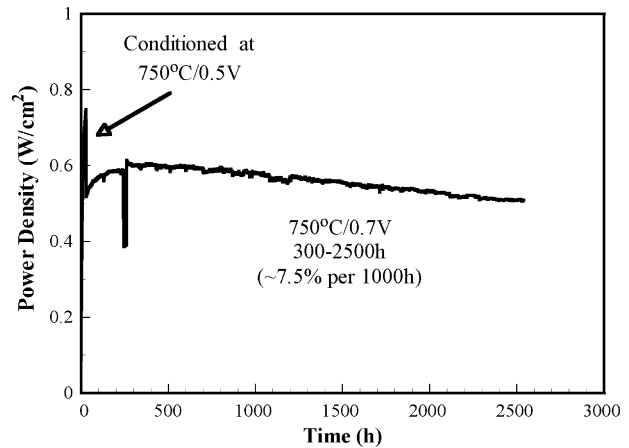

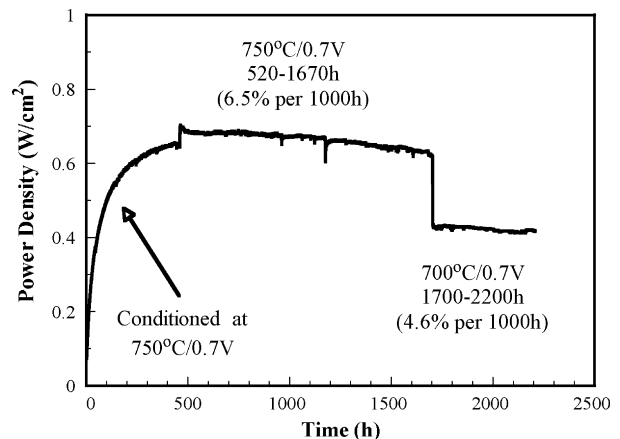Fig. 4. Influence of operating voltage (0.5 and 0.7 V) on Ag-LSCF conditioning at 700 °C.

Fig. 6. Long-term performance of anode-supported SOFC utilizing Ag-SSCo composite cathode (750/0.7 and 700 °C/0.7 V).
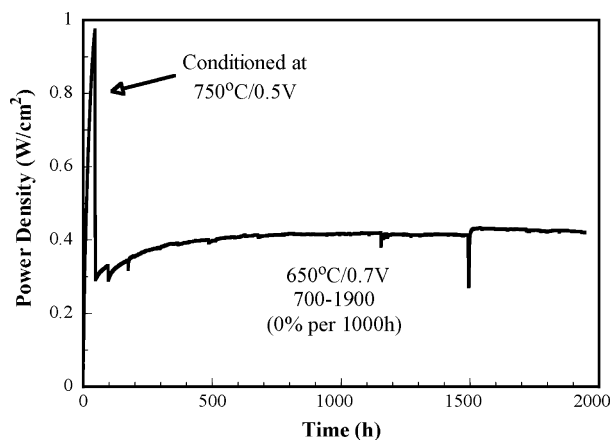
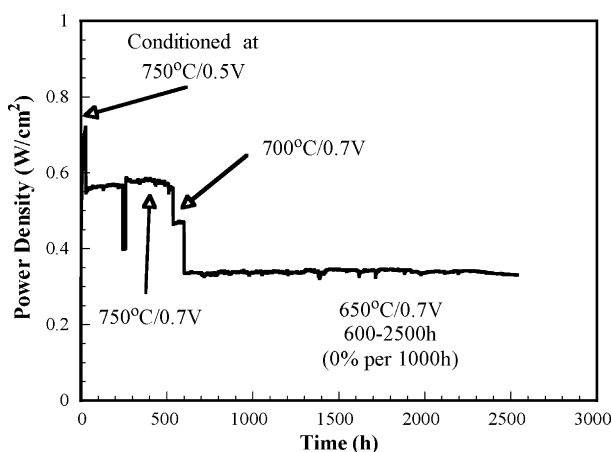Fig. 7. Long-term performance of anode-supported SOFC utilizing Ag-LSCF composite cathode (650 °C/0.7 V).

Fig. 8. Long-term performance of anode-supported SOFC utilizing Ag-SSCo composite cathode (650 °C/0.7 V).

4. Conclusion

The presented data indicate that silver spheres coated with LSCF and SSCo cathode powder (via a dry coating technique) provide reasonable power densities between 750 and 650 °C (500–650 mW cm^{-2} at 750 °C/0.7 V, 400–450 mW cm^{-2} at 700 °C/0.7 V, and 300–400 mW cm^{-2} at 650 °C/0.7 V). The performance is characterized by initially low performance (<100 mW cm^{-2}) followed by substantial conditioning. Phenomena responsible for the conditioning characteristics of these appear to be related to the electromigration of silver along the SDC interlayer during cell operation thereby extending the triple phase boundary area. Cathode conditioning could be accelerated by operating at higher temperatures or lower voltages.

However, while no degradation was observed for a cell held at 650 °C for almost 2000 h, operation at 700 and 750 °C yielded power degradation rates of approximately 4.5 and 7.5%, respectively. The instability of the material is thought to be related to continued (and excessive) migration of the silver at the higher operating temperatures resulting in decreased triple phase boundary areas, and a restriction to air access to the cathode-electrolyte interface. The observed instability above 650 °C provides a significant impediment to the potential application of this material for intermediate temperature SOFCs operating from 650 to 800 °C. The performance at 650 °C is too low to consider using this material in an SOFC operated at that temperature, and operation at higher temperatures leads to degradation rates that are unacceptably high for stationary and automotive applications.

In addition the practicality of such a material is questionable since it is subject to long conditioning times, and the conditioning relies on a drastic morphology change that may not be easy to control to provide reproducible conditioning and power density characteristics. However, on a more positive note this study does demonstrate the potential use of silver (or silver composites) for low temperature SOFC cathodes. The key to its implementation would be to increase the low temperature performance and assess the possibility of inducing the desirable post-conditioned microstructure during processing.

Acknowledgements

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