Efficient Electro-Catalysts for Enhancing Surface Activity and Stability of SOFC Cathodes

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The search for a sustainable supply of clean and economical energy has stimulated great interest in fuel cells for direct conversion of chemical fuels to electricity. Among all types of fuel cells, solid oxide fuel cells (SOFCs) are the cleanest and most efficient ones with excellent fuel flexibility. They are capable of direct utilization of a wide variety of fuels, from hydrogen to hydrocarbons, coal gas, and bio-derived fuels. One of the technical hurdles to commercialization of SOFC technologies, however, is the high operating temperature that requires the use of expensive materials. The enhancement of cathode performance improvement can be further enhanced.

In this article, we report our findings in modification of an LSCF cathode using new electro-catalysts with higher ORR activity and better chemical stability: Pr$_{0.75}$Sr$_{0.25}$MnO$_3$ (PSM) and PrSrCoMnO$_{6-δ}$ (PSCM), including the interfacial polarization resistance (R$_p$), long term stability, and cathodic activation behavior of PSM- and PSCM-infiltrated LSCF cathodes under typical SOFC operating conditions. Both PSM and PSCM are derivatives of a doped lanthanide manganite, a family of cathode materials that has been widely studied for SOFC.

The similarity in crystal structure of PSM and PSCM to that of LSCF (perovskite) allows for facile formation of a conformal film coating of LSM enhanced both surface ORR activity and stability of LSCF cathodes. While the concept feasibility of surface modification has been demonstrated, the degree of performance improvement can be further enhanced.

In order to determine the phase composition of the catalysts coated on an LSCF cathode, PSM and PSCM powders were derived from the same solution used for solution coating. The X-ray diffraction (XRD) patterns in Figure 1a and Figure S11 indicate that PSM and PSCM (calcined at 900 °C for 1 h) have a simple and complex perovskite phase, respectively. A structural model for PSCM (Figure 1b) is proposed based on the estimated lattice parameters (Table S11). The Mn and Co ions (the B cations) are randomly distributed at the center of the BO$_6$ octahedrons. The Pr and Sr ions (the A cations) are at the center of the layers surrounded by tilted BO$_6$ octahedrons. The chemical compatibilities between PSM, PSCM, and LSCF under actual synthesis conditions were also investigated. The mixtures were obtained by dispersing LSCF powders in the PSM and the PSCM solution, followed by drying and annealing the resulting powder mixtures at 900 °C in air for 500 hours.

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There was no evidence of any secondary phases in the XRD patterns for either case, suggesting that PSM and PSCM both have excellent phase stability against LSCF under the conditions studied.

Possible chemical interdiffusion between the PSM/PSCM catalysts and LSCF substrate were further investigated by annealing the powder mixtures at 1000 °C in air for 100 hours and analyzing the resulting products using Raman spectroscopy. Figure 1c shows parts of Raman spectra collected from LSM-LSCF, PSM-LSCF, and PSCM-LSCF mixture samples before and after annealing. In each of the samples, the broad set of Raman bands between 600 and 750 cm⁻¹ correspond to vibrations involving the B ions and oxygen ions in the bulk material. In the LSM-LSCF spectrum, this band is nearly symmetric in character. After annealing, the band retained its shape but its center shifts slightly from 668 to 662 cm⁻¹, corresponding likely to some exchange of Mn, Co, and Fe ions in the bulk material during the course of the annealing. Similar inter-exchange was observed in LSM-coated LSCF samples, where an “LSMCF” inter-phase was formed between LSM and LSCF. In the PSM-LSCF and PSCM-LSCF spectra before annealing, the left side of this band was slightly more prominent. After annealing, however, the right shoulder of the band (694 cm⁻¹) became more pronounced, indicating a greater distortion in the lattice than in the LSM-LSCF case that was due likely to changes in the A-site ions. In similar materials, this Raman band changed similarly when different ions were doped in the A-site. Therefore, in the PSM-LSCF and PSCM-LSCF cases, some inter-exchange likely took place between the Pr, La, and Sr ions, likely leading to the formation of a “LPSMCF” perovskite phase. However, there was no evidence in the Raman analysis that might suggest the formation of any undesirable, non-perovskite secondary phase.

Figure 2a and 2b shows the typical surface morphologies of a blank LSCF surface and a PSCM coated LSCF surface. Grains of the blank LSCF are very smooth with clear triple junctions. With PSCM coating, the continuous and dense film is visible on the surface of LSCF grains, making it appear rougher and very different from the typical microstructures of particle-coated cathode surface. It is also noted that there is clear contrast across different grains due possibly to the differences in orientation of the PSCM films inherited from the underlying LSCF grains. When these catalysts were coated on the surface of a porous LSCF cathode through a solution infiltration process, they appear similar (Figure 2c and 2d). The thickness of the thin-film coating was estimated from the following equation:

\[
L = \frac{VCM}{\rho S}
\]

where \( V \) is the volume of the solution, \( C \) is the solution concentration, \( M \) is the molar weight of the catalyst used for coating, \( \rho \) is the theoretical density of the infiltration material, and \( S \) is the inner surface area of porous cathode that was coated with the solution. When \( V, C, \) and \( S \) were held constant, the thickness \( L \) is determined mainly by the ratio of \( M/\rho \), which is similar for LSM, PSM, and PSCM (varied from 35 to 37 mol cm³ g⁻²). Therefore, it is reasonable to assume that the thicknesses of the
PSM and PSCM coatings are comparable to that of the LSM coating on LSCF, which was determined to be in the range of 2 to 23 nm by careful TEM analysis.\(^{[26]}\)

The electrochemical behavior of the catalyst-infiltrated LSCF cathodes was characterized at 750 °C under open circuit conditions using impedance spectroscopy (Figure 3a). Unlike the LSM-infiltrated LSCF cathode, which had higher impedance than the blank LSCF cathode, the PSM-infiltrated LSCF cathode displayed smaller impedance than the blank LSCF cathode. Clearly, the PSM-infiltrated LSCF has higher catalytic activity for ORR than the LSM-infiltrated LSCF cathodes. The PSM coating significantly reduced the interfacial polarization resistance \(R_p\) of the LSCF cathode even under open-circuit voltage (OCV) condition in contrast to the LSM infiltration. The PSCM infiltration further decreased \(R_p\) at the same concentration of infiltration. For example, \(R_p\) was 0.107 and 0.093 \(\Omega\) cm\(^{-2}\) for the PSM and PSCM infiltrated LSCF cathodes, contrasting with the 0.126 and 0.197 \(\Omega\) cm\(^{-2}\) for the blank LSCF and LSM infiltrated LSCF cathodes at 750 °C. Figure 3b shows the temperature dependence of \(R_p\) for these catalyst-infiltrated LSCF cathodes. At an intermediate temperature range, the PSCM infiltration provided the lowest \(R_p\) among these Mn-containing catalysts. All of the curves appear to have similar slopes, indicating that the primary ORR mechanism remains the same. We employed symmetrical cells with a three-electrode configuration to evaluate the polarization behavior. Unlike LSM infiltration, the PSM and PSCM infiltrated LSCF cathodes initially showed lower \(R_p\) compared to blank LSCF cathodes (Figure 3c), followed by a fast reduction in \(R_p\) at a given cathodic overpotential, which is likely associated with the higher electrocatalytic activity (Figure S13, S14 and S15) as well as stronger activation behavior (Figure S16) for PSM and PSCM. This suggests that PSM and PSCM infiltration are able to further enhance performance under operation conditions.

Shown in Figure 4a is the typical performance of button cells infiltrated with different catalytic coatings and operated at 750 °C under a constant cell voltage of 0.7 V. Within 550 hours, the cells with the PSCM-infiltrated LSCF cathodes showed the best performance with significant activation behavior. Compared to the cells with LSM and PSM infiltration, the PSCM infiltrated cells showed a gradual increase in performance, implying a continuous activation during operation. The “long-term activation” effect could counter against other degradation mechanisms and stabilize cell output. This phenomenon has attracted our attention for further study. After over 500 hours of operation, the performance enhancement (compared to that of the cell with a blank LSCF cathode) was 41.6%, 51.5%, and 61.7% for LSM, PSM, and PSCM infiltration, respectively. Due to possible degradation of the blank LSCF cathode during operation, an even larger performance difference would be expected for operation over a longer period of time. The degradation rate of the cell with the blank LSCF cathode in this study was −0.035% per hour, considerably lower than 0.06% per hour reported by others\(^{[22]}\) under similar conditions. The current-voltage characteristics and the corresponding power densities for the cells with or without infiltration are quite different (Figure 4b and 4c). In comparison with the LSM-infiltrated LSCF cathode, PSM- and PSCM-infiltrated LSCF displayed stronger enhancement in activity and stability of full cells, which may be attributed to higher intrinsic electro-catalytic activity, stronger activation, and desirable cation inter-diffusion between infiltrates and LSCF backbone.

In conclusion, both electro-catalytic activity and stability of the state-of-the-art LSCF cathode have been enhanced by more active Mn-based catalyst coatings as demonstrated in symmetrical and anode-supported cells. Further, the infiltration process used to apply the coating is simple and economically feasible for application to commercial cells. First, the catalyst coating is very thin; in fact, an ideal thickness of the Mn-based catalyst coating is only about 10 to 50 nm, far thinner than other cell components such as the anode support (0.3–0.7 mm), electrolyte (10–20 μm), or cathode backbone (50 μm). This implies that other catalytically active materials, such as Pr- or Pd-containing ones, which are too expensive to use as bulk cathode material, may become economically feasible. It is worth pointing out that Pr-containing Mn-based catalysts studied in this work are superior in activity and stability enhancement over LSM. Second, compared with most infiltration cases where multiple steps are needed to increase loading in order to obtain sufficient conductivity for optimal performance, our infiltration process is more efficient (one step), making it possible to be readily implemented in typical SOFC fabrication.

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Figure 2. Surface morphology of blank and catalyst-coated LSCF: Typical surface views (SEM images) of (a) an LSCF pellet fired at 1350 °C for 5 hours; (b) a PSCM coated LSCF pellet annealed at 900 °C for 1 hour; (c) a porous LSCF cathode fired at 1080 °C for 2 hours; and (d) a PSCM-coated LSCF cathode fired at 900 °C for 1 hour.
Experimental Section

Preparation of LSM, PSM, and PSCM Solution for Infiltration:

Stoichiometric amounts of high-purity praseodymium nitrate hydrate, lanthanum nitrate hexahydrate, strontium nitrate, cobalt nitrate hexahydrate, and manganese nitrate hydrate (all from Alfa Aesar) were dissolved in a mixture of deionized water and ethanol (at a volume ratio of 1:1) to form 0.1 mol L\(^{-1}\) solution. 5 wt.% polyvinyl pyrrolidone (PVP) were added to the solution as a surfactant and a stoichiometric amount...
of glycine was added as a complexing agent and the fuel for subsequent self-combustion. 5 μL of the stock solution was deposited on the as-prepared LSCF surface or a porous cathode. After overnight drying in ambient air, the resulting coating was fired at 900 °C in air for 1 h.

Fabrication of Symmetrical Cells and Test Cells with Three-Electrode Configurations: YSZ pellets were prepared by uni-axially pressing commercially available YSZ powders (Daiichi Kigenso, Japan) followed by sintering at 1450 °C for 5 h to achieve relative density of ~98%. LSCF (FueCell Materials, US) green tapes were prepared by tape-casting, which were then bound onto both sides of a YSZ electrolyte pellet using a slurry of Sm₄₋₅Ce₂₋₅O₁₉ (SDC, the buffer layer). The cells were then co-fired at 1080 °C for 2 h to form porous LSCF electrodes (with an area of 0.3 cm²) on YSZ. The SDC powder was synthesized using a precipitation method (SDC, the buffer layer). The SDC powders were then dispersed in acetone with V-006A (Heraeus, US) as binder and ball-milled for 24 h to form a stable SDC slurry. The symmetrical cells were also tested in a three-electrode configuration. The LSCF cathode with/without catalyst coating were used as working electrode (WE) and counter electrode (CE), respectively. Pt paste was fired at 900 °C for 1 h as reference electrode (RE) by positioning it as close to working electrode as possible.

Fabrication of Anode-Supported Full Cells: Tape-cast NiO/YSZ anode-support was first fabricated and pre-fired at 850 °C for 2 h. Then, an active NiO/YSZ layer (~15 μm) and a YSZ electrolyte (~15 μm) were sequentially deposited on the anode support by a particle suspension coating process followed by co-firing at 1400 °C for 5 h.39 The LSCF cathode was then applied to the YSZ electrolyte using the same procedures as described earlier for the fabrication of symmetric cells.

Characterization of Phase composition and Microstructure of Cathode: The phase compositions of LSCF, PSM, and PSCM powders as well as their composites were determined by XRD. LSCF powders were fired at 1080 °C for 2 hours (the same as the fabrication process of the cathode backbone). PSM and PSCM powder precursor were firstly obtained from a glycine-combustion method and were then fired at 900 °C for 1 hour (the same as the fabrication process of their coating), and their composites were obtained by dispersing LSCF powders (1080 °C for 2 hours) in PSM and PSCM solution (powder weight ratio = 50:50) followed by drying in an oven and firing at 900 °C in air for one hour. Raman spectroscopy (Renishaw RM1000) was performed using 514 nm laser excitation on mixed PSM-LSCF and PSCM-LSCF samples after being annealed at 1000 °C for 100 hours for further chemical analysis. The microstructure and morphology of the LSCF pellets with/without catalysts coatings were examined using a scanning electron microscope (SEM, LEO 1530).

Electrochemical Measurements: The area specific resistances (ASR) of cathodes were measured in a two electrode symmetric cell configuration using two pieces of Pt mesh as current collector (without Pt paste to avoid its possible contribution to catalytic activity) at 500–800 °C. Impedance spectroscopy spectra were acquired using a Solartron 1255 LF analyzer interfaced with an EG&G PAR potentiostat model 273A with an AC amplitude of 10 mV in the frequency range from 0.1 kHz to 0.1 Hz. The overpotential, η, was calculated using the following equation:

$$\eta = U_{WR} - i R_{ohm}$$  (2)

$U_{WR}$ is the potential applied between WE and RE, $i$ is the corresponding current density, and $R_{ohm}$ is the ohmic resistance of the cell. The observed cell current response typically reached a steady state after the DC polarization was applied for ~30 min. To accurately determine the ohmic resistance of the cell, impedance spectra were also collected under identical DC polarization after the cell response was stabilized. The button cells were mounted on an alumina supporting tube for fuel cell testing at 750 °C with humidified hydrogen (3% H₂O) as the fuel and stationary air as the oxidant. The cell performance was monitored with an Arbin multi-channel electrochemical testing system (MSTAT).

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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