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Synthesis of nanocrystalline lanthanum manganite with tailored particulate size and morphology using a novel spray pyrolysis technique for application as the functional solid oxide fuel cell cathode

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HIGHLIGHTS

- ► Spray pyrolysed nanocrystalline LSM possess tailored particulate size and morphology.
- ► Precalcined LSM nanoparticles used as seeding agent for in-situ particle growth.
- ► Tailored morphology of functional cathode results in lowest polarization (0.4 Ω-cm^2).
- ► Functional cathode enhances cell performance appreciably (3.2 A cm^{-2}, 0.7 V & 800 °C).
- ► Functional cathode also reduces cell ASR down to 0.109 Ω-cm^2 at 800 °C.

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ABSTRACT

Nanocrystalline strontium doped lanthanum manganite ($La_{0.65}Sr_{0.3}MnO_3$) having variable particulate sizes and morphology is synthesized by a novel spray pyrolysis (SP) technique for solid oxide fuel cell (SOFC) cathode. Precalcined nanopowders received from the first SP run are added as the seeding agent in the subsequent runs for their in-situ growth inside the reactor. The suitability of the nano and micro particulates having interconnected porosity are examined as cathode functional and current collection layers. Detailed physical, microstructural and bulk electrical characterizations of such nanopowders are studied. Cathode polarization behavior and the associated rate limiting steps are characterized using AC impedance spectroscopy in the symmetric cell configurations. The optimization of the cathode processing conditions has brought the interfacial polarization down to ~0.2 Ω-cm^2 and thereby increases the cell performance from 2.0 to 3.2 A.cm^{-2} (0.7 V, 800 °C). Such improvement in anode-supported SOFC is correlated with the cathode processing conditions, particulate size, morphology and cathode microstructure.

1. Introduction

The transition from electrolyte supported to electrode-supported designs has induced significant affirmative aspects in the development of solid oxide fuel cells (SOFCs). Electrode-supported cells are categorized into cathode and anode-supported cells. Between these two types, anode-supported cells having thin electrolyte (10–30 μm) can be operated at much lower temperatures of 600–800 °C [1]. The ohmic loss for such thin electrolyte is found to be negligible for the cell operating at 700–800 °C. The cathode polarization can be minimized by lowering the SOFC operating temperature [1]. Therefore, selection of appropriate cathode material is important to improve the cell performance [2]. Electrode kinetics is also found to be retarded upon reducing the cell operating temperature and thereby enhances the interfacial polarization resistance. This eventually affects the oxygen reduction reaction (ORR) at the cathode. High catalytic activity for oxygen reduction is maintained at the cathode for its effective performance as the oxygen reduction electrode [3]. In general, materials having mixed ionic and electronic conductivity (MIEC) reduce the cathode polarization related to the electrochemical reduction of oxidant [4,5]. The composite of Sr-substituted $LaMnO_3$ (LSM) and 8 mol% yittria stabilized zirconia (YSZ) is found to be the most widely used cathode for SOFC application [4]. While LSM–YSZ provides good performance at ~800 °C, the interfacial

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polarization at the cathode–electrolyte junction reduces rapidly with higher cell operating temperature. Inhomogeneous cathode microstructure within the cell also causes a non-uniform current distribution during cell operation that leads to variation of local current density at the cathode. This inhomogeneity results in further microstructural degradation with lower cell performance [4]. The inhomogeneous cathode microstructure is responsible for compositional changes by chemical reactions; grain growth and delamination at the cathode-electrolyte interface [6–8]. In addition, stability of the cathode-electrolyte interface plays an important role in minimizing the electrode polarization [9,10]. It is well known that, the formation of $La_2Zr_2O_7$ through high temperature interaction between $La_{1-x}Sr_xMnO_3$ and YSZ increases the cathode-electrolyte interface polarization resistance [2,11]. Several groups of researchers have studied the overpotential of LSM based cathode current collection layer and LSM–YSZ composite cathode reaction layer at temperatures $\geq$800 °C [12,13]. The interfacial resistance (R_i), measured at a definite temperature, is found to drop as the YSZ/LSM weight ratio is increased to ~1.0 [14]. Nanoporous cathodes are expected to exhibit a lower cathodic overpotential because of the availability of large effective surface area for electrocatalytic reactions. But such cathodes are generally vulnerable to degradation at high temperatures. Owing to such features, short-term performances of cells having such cathodes are superior compared to their long-term activity [15]. For better cell performance, nanocrystalline cathodes having significant catalytic activity with desired particulate sizes and morphologies are found to be the crucial [16]. Detailed investigation has been carried out on samarium strontium cobaltite (SSC) cathode system based on the control of particulate morphology and cathode microstructure and their effect on the electrochemical performance [17]. It is observed that, nanocrystalline cathode structures developed from nanopowders having mesoporosity induce higher rate of oxygen diffusion at cathode surface and hence reduce the polarization losses of the cathode layer [18,19]. Synthesis of the nanocrystalline cathodes have been studied by sol–gel, glycine-nitrate, impregnation, pulsed laser deposition or radio frequency (RF) sputtering etc. [20–24]. Spray pyrolysis (SP) is still considered to be one of the most effective methods for synthesizing nanocrystalline cathodes. The prime advantages of SP involve easier technique for synthesizing the multicomponent oxides in a single step according to the applicability, better homogeneity in nanoscale and up-scalability [25].

Under the present investigation, influence of particulate size and morphology of nanocrystalline $La_{0.65}Sr_{0.3}MnO_3$ (LSM)-based cathodes prepared by spray pyrolysis technique is studied in details. A unique approach is adopted using a novel low temperature spray pyrolysis technique for synthesizing nanopowders of LSM to be used for SOFC cathode functional layer (CFL) and cathode current collection layer (CCCL) application. Attempt has been made to add SP derived precalcined LSM nanopowders in the precursor solution as the seeding agent during subsequent runs of the pyrolysis. Use of such precalcined LSM powder as a seed material for in-situ growth inside the reactor during the pyrolysis reaction may lead to the formation of porous micro granules of LSM with different particulate morphology. A comprehensive effort is made to understand the material properties of such SP synthesized nano and micro LSM powders having different particulate size and morphology. Detailed electrical characterizations and polarization behaviors are studied using DC electrical conductivity and electrochemical impedance spectroscopy (EIS) measurements to correlate the polarizations of SP synthesized cathodes with the particulate size and morphology. Finally, electrochemical activity of the optimized cathode composition is studied in the form of current–voltage relationship for SOFC single cell. A clinical correlation is also described among cell performance, cathode particulate size, morphology and cell microstructure.

2. Experimental

2.1. Synthesis, preparation and characterization of LSM and LSM–YSZ cathode powders

For the preparation of Sr-doped lanthanum manganite ($La_{0.65}Sr_{0.3}MnO_3$) composition, lanthanum nitrate hexahydrate (Sisco Research Laboratory Pvt. Ltd., India, >99.0%), strontium nitrate (s. d. fine chem. Ltd., India, >99%), manganese (II) acetate tetra hydrate (E Merck India Limited, >99.5%) and citric acid monohydrate (E Merck India Limited, Mumbai, India, >99.5%) were used as the precursor materials. Stock solutions of lanthanum nitrate hexahydrate and strontium nitrate were prepared having different molar concentrations viz. 0.2 M, 0.5 M, 0.75 M and 1.0 M and were used as the nitrate precursor solutions. Stoichiometric amount of the metal nitrate solutions (N) and the acetate salt of manganese were mixed together to form the precursor salt solution. Citric acid monohydrate (C) was used both as chelating agent and fuel (in the combustion reaction) and was added to the above precursor salt solution so as to have a C/N ratio in the range between 0.5 and 0.6. The precursor solution was sprayed into the reaction zone of an indigenously made pyrolyser using a peristaltic pump and the two fluid nozzle assembly. The inlet temperature of the spray unit was maintained at 400 °C. The ashes generated as a result of the auto-combustion reaction was collected in cyclonic separators as coarser and finer fractions respectively. Gaseous reaction products such as NO_x, CO_2 etc. were scrubbed out by passing out the same through a scrubber attached at one end of the system. A schematic of the spray pyrolysing set up is given in Fig. 1. In order to have sufficient particulate growth during the pyrolysis reaction, batches were also formulated with a definite amount of addition of precalcined ashes derived out of the previous pyrolysis into the precursor solution as the seeding agent. The as-synthesized powders received from the first run of 0.25 M solution was added as seeding agents to the precursor solution having concentration range from 0.25 M to1.0 M of the precursor solutions for the subsequent runs. The particulate loading were kept constant at 25 wt % of the theoretical yield of 0.25 M precursor solution. Various LSM batch formulations thus prepared under the present investigation are given in Table 1. The synthesized powders were calcined at a temperature of 950 °C for 4 h. The phase identification of the as-prepared and the calcined LSM powders was confirmed by X-ray powder diffraction (XRD) data collected at a scan rate of 2° min^{-1} from X-ray diffractometer (Philips X'pert, PANalytical, Netherlands) with Cu-Kα radiation. Rietveld refinement of the diffraction data was carried out by PANalytical X'Pert High Score software using a pseudovoight function. The morphologies of the SP powders prepared under various synthesis conditions were examined by field emission scanning electron microscopy (FESEM – Gemini Supra 35, Zeiss). Brunauer–Emmett–Teller (BET) surface area of the powders was also characterized using a surface analyzer (Nova 4000 E, Quantachrome, USA). In addition, the particle size of the synthesized powders was also determined from the results of BET surface area. Among the synthesized compositions mentioned in Table 1, optimized LSM powders were selected based on particle size and morphology, to be used as cathode functional layer (CFL) and cathode current collection layer (CCCL) in the single cells. The primary selection criterion of LSM for CFL was, to have close proximity with that of particle size of 8YSZ (Tosho Corporation, Japan; d_{50} ~ 0.2 μm) having nanocrystallinity and interconnected porosity. Cathode functional layer was prepared upon mixing the optimized LSM with 8 YSZ for 4 h in a planetary mill (Fritsch,