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Preparation and evaluation of mechanochemically fabricated LSM/ScSZ composite materials for SOFC cathodes

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Abstract

The LSM/ScSZ composite powder materials for SOFC cathodes were prepared by the mechanical method using an attrition-type particle composing machine and their electrochemical performance was examined. They are designed in such a way that relatively large LSM particles are coated with fine-grained ScSZ particles prior to the electrode fabrication process such as sintering, thus ensuring the establishment of both the ionic and electronic conducting paths within the electrode. The composite cathode using these composite powders outperformed, in the interfacial area specific resistance, a simple LSM cathode and the LSM/ScSZ composite cathode fabricated by an ordinary starting powder mixture without mechanical treatment. The interfacial area specific resistance was actually reduced by 75% relative to the simple LSM cathode, and by 50% relative to the ordinary composite cathode. In addition, the amount of ScSZ doping was reduced down to 20% by weight fraction. The present result suggests that the proposed composite particles can be considered as a potential cathode material in order to enhance SOFC cathode performance.

Keywords: SOFC; LSM; ScSZ; Composite cathode; Mechanochemistry; Microstructure

1. Introduction

The strontium doped lanthanum manganite, or LSM cathodes with an addition of ion-conducting material such as yttria stabilized zirconia (YSZ) or scandium stabilized zirconia (ScSZ) are considered as one of the effective measures to enhance electrochemical performance of solid oxide fuel cells [1,2]. Kenjo and coworkers [3,4] demonstrated earlier the concept of the electrocatalyst–electrolyte composite electrodes in an attempt to increase an effective triple-phase boundary (TPB) region. Their $LaMnO_3$/YSZ composite cathodes actually showed significant improvement in polarization performance when compared with simple $LaMnO_3$ electrodes.

This doping effect of YSZ is featured as the increased electrochemically active $LaMnO_3$/YSZ interfaces formed inside the electrode, and the suppression of highly resistive $La_2Zr_2O_7$ formation at the electrode/electrolyte interface [4]. Also, the addition of fine-grained YSZ particles suppresses the grain growth of LSM particles, thereby improving long term durability [5]. Furthermore, it can be considered that the fine electrolyte particles ensure the contact between the cathode and electrolyte layers.

For the fabrication of composite electrodes, the important parameters to control the microstructure of composite cathodes are the grain size of starting powders, the weight ratio of lanthanum manganite and stabilized zirconia, and sintering temperature [4,6,7]. In the present study, the LSM/ScSZ composite powder mixture prepared mechanochemically was considered in order to give an additional measure to control the microstructure of composite cathode.

In the mechanochemical processing for powder production, the compression and friction forces applied to powder materials can result in solid phase reactions. Examples are the synthesis of lanthanum manganite type cathode materials or $LaCrO_3$ by grinding constituent oxides [8–10], and the fabrication of NiO/YSZ composite particles [11]. In addition, the other application of mechanochemical techniques is reviewed in [12]. As for the

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application of composite particles to SOFC cathode, Fukui et al. demonstrated the possibility of LSM/YSZ particles prepared by spray pyrolysis [13]. However, no attempt in fabricating LSM/ScSZ composite powder material using mechanochemistry for SOFC cathode has been reported.

The structural design concept of mechanically composed LSM/ScSZ powder material here is to form LSM particles covered by fine ScSZ powder, with sufficiently strong adhesion to the LSM surfaces in order to keep the structure effectively remaining in place during the electrode fabrication process. This composite powder is expected to ensure the creation of LSM/ScSZ interfaces inside the electrode, and to effectively form both the ion-conducting and electronic-conducting networks within the electrode. It is considered, in particular, that the added ScSZ can be utilized under controlled conditions, thereby minimizing the amount of ScSZ doping. Although conventional LSM/ScSZ composite cathodes are constructed in such a way that the ion conducting path within the electrode can be established as broad as possible, we tentatively considered here an electrode design with the ion conducting path at its required minimum in order to magnify the importance of control in the ionic path networking.

The present study concerns the preparation of the LSM/ScSZ composite powders by using the mechanochemical process and their effect on the improvement in cathode performance. In particular, the effect is viewed with an aspect to control the morphology of electrode microstructure.

2. Experimental

2.1. Particle composing machine using the mechanical method

The attrition type particle composing machine used here consists of a cylindrical containment vessel, inside of which a rotary blade in oval cylinder shape is set. While the blade rotates, powder material in the vessel undergoes compression and attrition forces at the gap between the rotary blade and inner surface of the vessel. The heat generated due to attrition force was rejected through water cooling so that the external metal surface temperature could be kept below 150 °C.

In preparation of composite particles, LSM/ScSZ powder mixture of 50 g per batch, with the weight ratio of LSM/ScSZ = 80:20, was dosed in the vessel and processed in an atmospheric condition. The rotary blade was driven by a motor at the rotation speed ranging from 2000 to 5000 rpm, which varied depending on the state of progress in particle composing as well as the starting powder mixture characteristics. The electric power required for motor shaft driving was manually controlled at a constant level, i.e. 1.5 kW or 3 kW, to keep the attrition force unchanged. After every 5–10 min operation, a powder sample was collected from the vessel and then operation was resumed. This sequence was repeated until cumulative process duration time reached typically 40–60 min.

2.2. Preparation of composite samples

Strontium doped lanthanum manganite, or LSM ($La_{0.8}Sr_{0.2}MnO_3$) powders with different particle sizes were supplied by Seimi Chemical Co., Ltd. The median particle diameter of these powders was measured, using the laser diffraction/scattering method, as D_{50} = 5.3, 4.4, (2.3), 2.0, 1.2, 1.0 and 0.5 μm. Here, the powder with D_{50} = 2.3 μm was used only for the purpose of observation for composite samples in Fig. 4. Ceria doped scandium stabilized zirconium (10Sc1CeSZ or ScSZ) was provided by Daiichi Kigenso Kagaku Kogyo Co., Ltd. with particle size; D_{50} = 0.5 μm. This ScSZ powder appears to be in the form of agglomerates with its primary particle diameter in the order of sub-microns. Several combinations of LSM/ScSZ powders were examined to prepare LSM/ScSZ composite particles. The samples were investigated by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). In addition, electrochemical performance as cathode material was determined by the interfacial area specific resistance (ASR) measurement in a half-cell arrangement.

2.3. Electrochemical measurement

The composite particle samples were manually mixed with ethyl cellulose 10 cps (Wako Pure Chemical Industries, Ltd.) in a mortar, with further addition of solvent, TMS-1 (Tanaka Kikinzoku). The prepared paste was screen-printed onto one side of a ScSZ electrolyte pellet of 15 mm in diameter and 2.2 mm in thickness, and then sintered at 1200 °C for 3 h. Its effective cathode area was 0.28 cm^2 with a thickness of 10 μm. For the counter electrode, Pt paste was screen-printed onto the other side of the pellet. Also, as a reference electrode, Pt wire was bound around the radial surface of the pellet at the position of half the thickness. Note that the electrolyte pellet was fabricated by powder pressing and was sintered in air at 1400 °C for 3 h, prior to the above screen-printing process.

For comparison purposes, a simple LSM cathode and LSM/ScSZ composite cathodes without using mechanically fabricated composite powder were also prepared as baselines.

AC impedance measurements were made in oxygen at 1000 °C and OCV, using an electrochemical measurement system; SI-1287 Electrochemical Interface and SI-1255B Frequency Response Analyzer (Solartron), and the interfacial resistance was evaluated in the form of ASR (Area Specific Resistance). In addition, the measured impedance spectrum was analyzed for an equivalent circuit model using Zview software (Schribner Associates Inc.).

3. Results

3.1. Observation of composite particles

Fig. 1(a) and (b) show the typical SEM images of an untreated LSM/ScSZ powder mixture and its composite powder. For the starting powder materials, the median particle diameter was D_{50} = 5.3 μm for LSM, and D_{50} = 0.5 μm for ScSZ, respectively. The starting ScSZ powder exhibited agglomerates consisting of sub-micron primary particles, and was dispersed onto large LSM particles of 3–6 μm. For the composite powder, after processed at the motor power of 1.5 kW for 60 min, the LSM particle surface was covered by ScSZ primary particles, with the