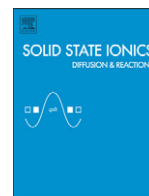




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Preparation of nano-structured cathode for protonic ceramic fuel cell by bead-milling method

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ABSTRACT

We developed a nano-structured Sm_{0.5}Sr_{0.5}CoO₃ (SSC55) cathode from slurry dispersed nanoparticles using a planetary bead-milling method. In order to evaluate the cathode performance, the cathode resistances and the protonic ceramic fuel cell properties were examined using electrochemical cells with a BaCe_{0.6}Zr_{0.2}Y_{0.2}O_{3-δ} electrolyte disk at intermediate temperatures. The cells with a milled SSC55 cathode showed lower cathode resistance and higher power density compared to those with the SSC55 cathode prepared from the conventional method. The improvement is attributed to an increase in the cathode reaction sites caused by the use of the smaller particles and a good adhesion to the electrolyte surface.

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1. Introduction

Solid oxide fuel cell (SOFC) has received considerable attention because of the prospective for efficient electricity generation. High operation temperature allows fast electrode reaction and mass transport, resulting in high energy conversion efficiency. However, such high-temperature operation causes degradation of components and limits the materials composing SOFC, and thus the reduction of the operation temperature is desired. Protonic ceramic fuel cell (PCFC) has attracted much attention for the advantage that the cells can work at an intermediate temperature (400–600 °C) [1–4]. Mixed oxide ion and electron conductors (MIEC) with perovskite materials are used as cathodes for SOFC and PCFC. Since the electrode reaction takes place at a triple-phase boundary of electrode, electrolyte and gaseous phases, the interface between the electrode and electrolyte is important for the electrode reaction. For PCFC, some studies have attempted to prepare composite cathodes of MIEC and the electrolyte materials in order to increase the contact area of the electrolyte/cathode interface [5,6]. Reduction of the particle size is also effective in increasing the contact area, and the cathodes are made by spray coating or spray pyrolysis using particles or precursors of the electrode substances prepared by wet chemical methods,

such as a sol–gel method, to spray [7–9]. In other reports, the cathode is prepared by a thin film deposition technique under high vacuum, such as pulse laser deposition and chemical vapor deposition [10,11].

We have developed a preparation of the perovskite oxide nanoparticles by pulverization using a planetary bead-mill [12,13]. This method has advantages, such as the easiness to handle of the starting material and the availability of a wide variety of materials.

This paper reports the preparation of the cathode for PCFC originated from the planetary bead-milled perovskite oxide nanoparticles. The comparison of the electrochemical properties between the cathodes made from as-baked material via solid state reaction and the bead-milled one, focuses on the effect of the original particle size of the cathode, in the PCFC performance.

2. Experiments

BaCe_{0.6}Zr_{0.2}Y_{0.2}O_{3-δ} (BCZY622) was chosen as a proton-conducting electrolyte. The electrolyte disk for cathode resistance measurement was prepared by a solid state reaction from BaCO₃, CeO₂, ZrO₂ and Y₂O₃, finally sintered in air at 1700 °C. The electrolyte for PCFC evaluation was prepared by a sol–gel method to ensure a sufficient gas tightness from the aqueous solution of each nitrate (Ba(NO₃)₂, Ce(NO₃)₃ · 6H₂O, ZrO(NO₃)₂ · 2H₂O and Y(NO₃)₃ · 6H₂O) mixing with citric acid monohydrate, EDTA and ammonium aqueous solution. The disk was sintered in air at 1600 °C (relative density >95%).

Sm_{0.5}Sr_{0.5}CoO₃ (SSC55) was chosen as the cathode material and was prepared by a solid state reaction method. Sm₂O₃, SrCO₃ and Co₃O₄

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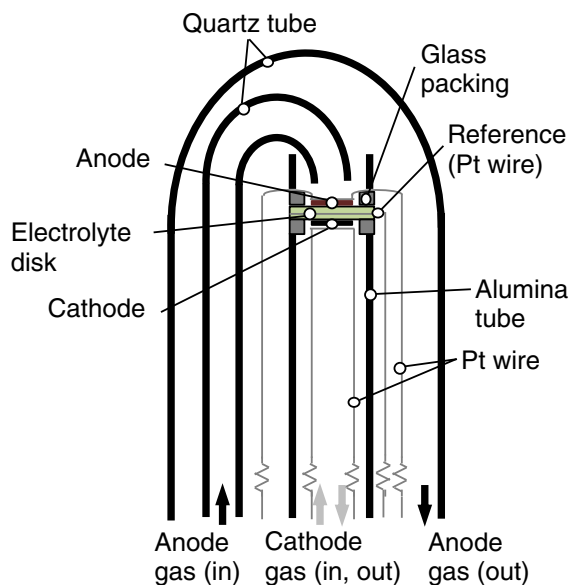


Fig. 1. Schematic image of the apparatus for electrochemical experiments.

were appropriately weighed, mixed in zirconia mortar with ethanol and calcined at 1000 °C for 10 h in air. Planetary bead milling (P-7, Fritsch) was performed for the SSC55 thus prepared to reduce the particle size. 1 g of the powder was pre-milled with 2-mm- ϕ zirconia balls at 500 rpm for 1 h, and then milled with 2-mm- ϕ zirconia beads at 800 rpm for 7 h using a zirconia pot (45 cm³) with 16.6 g of ethanol as a dispersant and 2.32 g of polyvinylpyrrolidone (PVP, m.w. = 220,000, 35 wt.% in water) as a binder. PVP was added to avoid the formation and development of cracks during drying and baking for the preparation of the SSC55 electrode. Dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern) measurement was performed on the obtained slurry to evaluate the particle size distribution. Powder XRD (Ultima IV, Rigaku) was measured for the slurry dried with infrared lamp. The SSC55 cathode was prepared by spin-coating the obtained slurry onto the BCZY622 disk (diameter = 13 mm ϕ , thickness = 0.5 mm). The SSC55 cathode prepared from the powder which did not experience the bead-milling was also made onto the BCZY622 by screen printing as a comparison. The diameter of the cathode was 8 mm ϕ . The microstructure of the cathode–electrolyte interface after heating at 950 °C was observed by a scanning electron microscope (SEM, SM-350, Topcon).

Fig. 1 shows the schematic image of the apparatus for electrochemical experiment [12–14]. The anode is a porous platinum for the cathode resistance measurement and Ni for the evaluation of PCFC characteristics. As the reference electrode, the platinum paste was applied on the rim of the disk. The sample disk was fixed on the alumina tube with Pyrex glass rings (thickness = 0.5 mm). Baking these electrodes and melting the glass ring as the gas seal were in situ after the sample was attached to the experimental apparatus at 950 °C. A platinum mesh (80 mesh) with platinum lead wires was used as the current collector

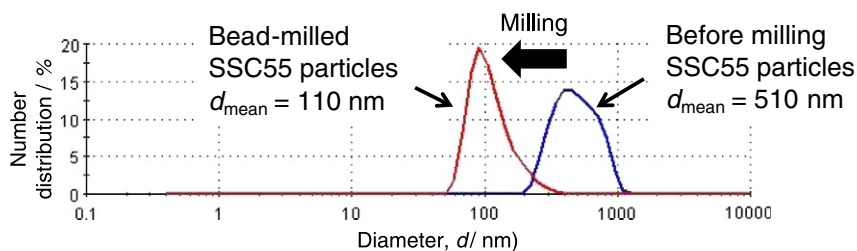


Fig. 2. The particle diameter distribution of SSC55 particles before and after bead milling measured by dynamic light scattering (DLS). Measurements were conducted on slurries diluted with ethanol.

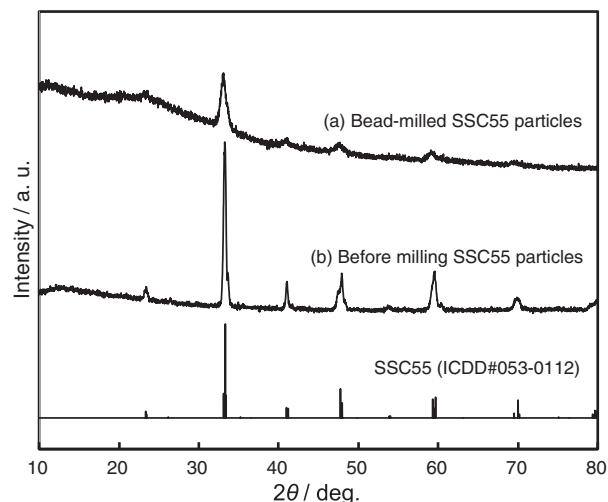


Fig. 3. XRD patterns of (a) powder obtained by drying the bead-milled SSC55 slurry and (b) as-calcined SSC55 powder.

for electrodes. A platinum wire was attached to the reference electrode by winding the wire on the rim with covered platinum paste. The cathode resistance was evaluated by AC impedance spectroscopy (VersaSTAT 3, Princeton Applied Research) in humidified air ($p(\text{H}_2\text{O}) = 0.019$ atm) at 600–800 °C. For the evaluation of PCFC properties, the current–voltage characteristics were measured at 600 °C with flowing humidified H₂ at the anode side and humidified air at the cathode side. Both of the humidified gasses are included in the water vapor ($p(\text{H}_2\text{O}) = 0.019$ atm).

3. Results and discussions

By planetary bead-milling of the SSC55, a viscous slurry was obtained. The slurry stays homogeneous and no precipitation takes place. This suggests a good dispersion of the milled SSC55 particles in an ethanol dispersant with PVP binder. Fig. 2 shows the particle size distribution of the milled slurry. The mean diameter is 110 nm, which is about 5 times smaller than that before milling. Fig. 3 compares the XRD patterns of bead-milled and as-prepared (not-milled) SSC55 powders; the bead-milled slurry was dried to obtain the powder for the measurement. The as-prepared SSC55 shows the pattern attributed to orthorhombic perovskite. After milling, the XRD pattern maintains the same crystal phase with no other peaks assignable to the formation of secondary phases. As shown in Fig. 3, the XRD peaks of the milled SSC55 became broader than those of the SSC55 before milling. The broadening of the peaks was due to the reduction of crystallite size. The SSC55 was grinded not only into secondary particles, such as agglomerated grain, but also into primary particles by the bead-milling method. On the other hand, it is possible to assume that the broadening of the XRD peaks is partly originated from the reduction of crystallinity taking place during milling since the milling gives a high attrition energy to

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