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Fabrication and characterization of microtubular and flattened ribbed SOFCs prepared by the multi-dip coating and co-firing

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Abstract

Presently, solid oxide fuel cells (SOFCs) are among the most efficient type of fuel cells and are expected to play a significant role in the next generation of energy conversion systems. Many types of SOFCs have been investigated in an effort to improve operational temperature tolerance. One particularly unique configuration is the microtubular cell, which has a large specific surface area per unit volume and can improve cell performance if integrated into stacks. In this paper, ceramic microtubular cells of diameter less than 1 mm were prepared via a multi-dip coating method. Steel wire was coated with polystyrene to make microtubular and flattened ribbed cells (FRCs). Green microtubular cells were separated from the wire by dissolving the polystyrene layer and co-firing at 1350 °C. These tubular cells show good linearity and a maximum power density of 0.14 W/cm^2 at 550 °C. This coating process can be easily automated in comparison to the conventional extrusion process.

Keywords: A. Dip coating; B. Microstructure-final; C. Electrical properties; D. CeO_2; E. Fuel cells

1. Introduction

The SOFC is a very promising candidate to be incorporated into electric power units and cogeneration systems in the next generation of power systems.[1–3] In particular, the tubular type SOFC has a long history of development by Siemens Westinghouse Power Corporation and has been investigated as a potential power unit by TOTO.[4,5] It is well known that tubular type SOFCs show good durability when subject to rapid heating cycles.[6] So far, the most common preparation process for tubular type cells is extrudable ceramic formulation due to its reliability. As can be seen in the report by Suzuki et al., these as-extruded soft microtubes are difficult to handle and special care is required to prevent damage.[7] In this present work, a new fabrication process for making microtubular cells with a diameter less than 1 mm using multi-dip coating was studied. The applied coating process is very simple and can be useful for preparing tiny ceramic parts when the appropriate coating parameters are identified. The large power densities per unit volume for the microtubular cells are derived from their large surface area through the integration of several cells as discussed in the literature.[8,9] In this study, the fabrication and characterization of LSM–GDC/GDC/NiO–GDC microtubular cells were investigated as a new process for mass production. Gadolinium doped ceria (GDC) used in this work serves as an electrolyte which can be used in an intermediate temperature range and is a promising candidate similar to other electrolytes such as LSGM, Sc doped zirconia, and Sm doped ceria.[2,3] We have studied the co-sintering of a three-layered flat cell of LSM–GDC/GDC/NiO–GDC prepared by tape casting, since the reaction between samarium doped ceria and LSM was not observed.[10,11] Electrical performance of the prepared microtubular cell was measured and was compared with that of a flat disc type cell. Possible ways to improve future cell performance will be discussed.

2. Experimental

2.1. Preparation of microtubular and flattened ribbed SOFCs

The experimental method used in this work is outlined in Fig. 1. First, aqueous slurries of electrolyte and electrodes were

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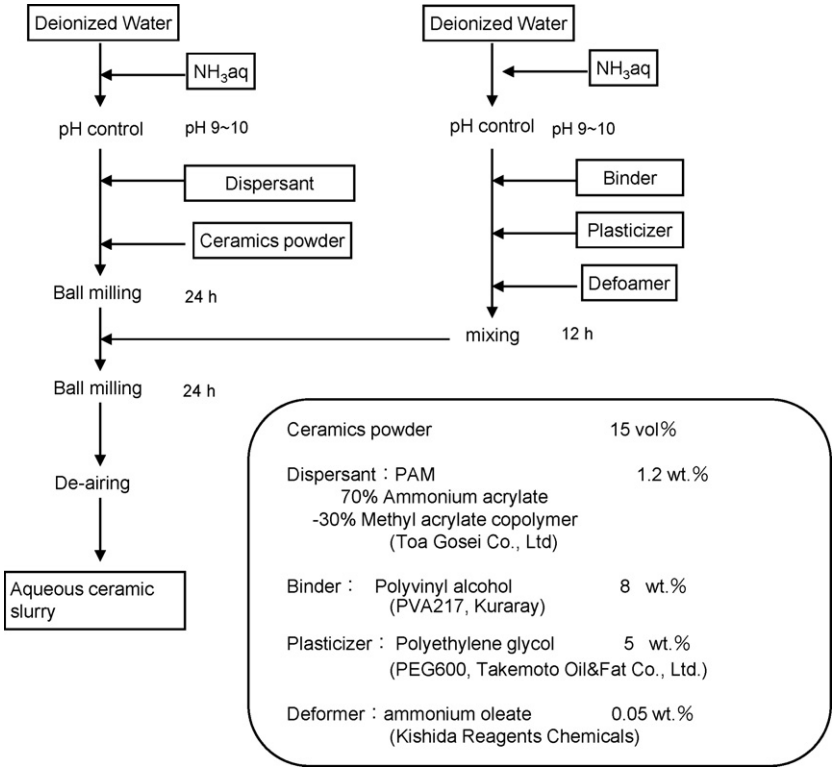

Fig. 1. Preparation process of aqueous ceramic slurries.

prepared by mixing ceramic powder, dispersant, binder, plasticizer, deformer with deionized water, and followed by ball milling as shown in Fig. 1. GDC powder (CGO 90/10 SY LSA, specific surface area: 11 m^2/g, Anan Kasei Co. Ltd.) was used. A mixture of 65 mass% NiO (Kishida Chemical Co. Ltd.,) and 35 mass% GDC powder was used for the anode material and a mixture of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) and 50 mass% GDC was used for the cathode material. The $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ powder was prepared via a solid state reaction using lanthanum, strontium and manganese carbonate, followed by planetary ball milling with ethanol. The slurries were processed in a hybrid mixer (HM-500, KEYENCE) to remove entrapped air, and were deposited onto steel wire ranging in diameter from 0.3 mm to 0.8 mm. In order to suppress the strong adhesion to the steel wire, the wire was pre-coated with a polystyrene polymer (PS, Kishida Reagents Chemicals) toluene solution as described in Fig. 2. The thickness of the electrodes and the electrolyte layer was controlled by adjusting the ceramic and binder contents in the slurries and coating times. Since it was difficult to obtain a sufficiently thick anode NiO–GDC layer from a single dip coating, the anode coating process was repeated twice to obtain a film approximately 100 μm in thickness. After coating, each layer was dried under well-controlled temperature and humidity conditions using a drying chamber (LH21-11P, Nagano Science Co. Ltd.,) After drying, the prepared microtube was removed from the steel by dissolving polystyrene layer in a toluene bath for 30 min. The prepared three-layered tube was set in a flat platinum container and then heat treated at elevated temperatures. The binder was burned out by slow heating up to 500 °C with a heating rate of 2 °C/min. After holding the temperature

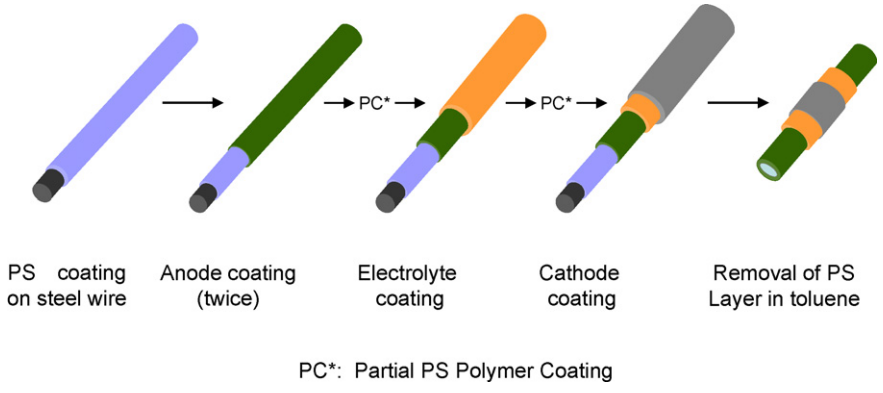

Fig. 2. Preparation of LSM–GDC/GDC/NiO–GDC microtubular cell by multi-dip coating.

at 500 °C for 2 h, the three-layered cell was sintered at 1350 °C for 4 h with a heating rate of 5 °C/min.

The same coating process was also used for the preparation of FRCs. Five of the anode coated wires were bundled together and coating with an anode and GDC electrolyte layer via dip coating in a GDC slurry.

2.2. Characterization

The viscosity of the prepared slurry was monitored as a function of powder and binder content using a viscometer (E-type, Tokyo Keiki Inc.). Coated and fired cells are subsequently imaged by the scanning electron microscopy (JSM5600, JEOL). Silver paste (TR-6182, Tanaka Precious Metal) was applied to the cathode of the tube to serve as a current collector and dried at 100 °C. Fuel-cell performance was measured using a Solartron 1255B and SI1287 system. A mixture of hydrogen and nitrogen humidified with water at 30 °C was used as the anode gas with a flow rate of 10 + 10 ml/min. Air was used as a cathode gas with a flow rate of 40 ml/min.

3. Results and discussion

3.1. Cell preparation

In this process, steel wire was coated with a polystyrene layer using a 5 mol% PS solution in order to separate the prepared multi-layered tube after drying, because the adhesion between steel wire and anode layer was too strong to separate after drying of multi-layer. Next, an anode layer of appropriate thickness was formed on the PS layer via control of powder and binder contents as summarized in Fig. 1. The viscosity of the cathode slurry used in this study was measured to be 440 mPa s. When diluted slurry was applied to this coating, the prepared anode layer became inhomogeneous and irregular. The prepared anode layer is, however, not thick enough to handle. Consequently, the anode coating and drying process was repeated resulting in an anode with a total thickness of 100 μm. The anode was then coated with GDC electrolyte layer with a thickness of 33 μm. A cross-section of the anode and electrolyte tube is shown in Fig. 3, demonstrating that a homogeneous coating was successfully achieved for this tubular cell. It is easy to control the thickness of each layer by changing the powder content of the slurry. The size of the cell is dependant on the coating conditions and the diameter of the wire. After the cathode layer was formed, the prepared multi-layer microtubular cell was co-fired at 1300–1350 °C. During the sintering process, the tubular cells shrank by almost 20%, yielding fired cells made from 0.8 mm steel wire with a final internal diameter of approximately 640 μm. Another important aspect of tubular cells is the linearity along the dipping direction. A prepared tubular cell with a length of 60 mm showed a bending length/tube length ratio less than 1% as shown in Fig. 4, which is straight enough to be interconnected with sealant.

An attempt to fabricate flattened ribbed cells (FRC) via the dipping process was also carried out. Fig. 5 shows the prepared FRC along with a cross-sectional view. To begin, five anode coated wires re-dipped in the anode slurry. Although the surface

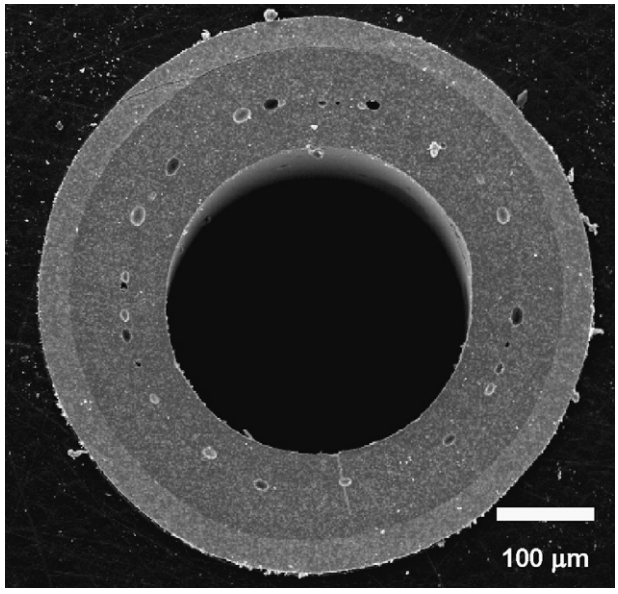

Fig. 3. Anode–electrolyte double layered tubular cell. Small pores were observed between first and second coating layers.

of FRC is smooth, the tubes still show large pores, yielding poor SOFC properties. Further study on the coating process is necessary in order to make a homogeneous and well-controlled microstructure for FRCs.

3.2. Cell performance

Co-fired tubular cells with inner and outer diameters of 615 μm and 970 μm were characterized. The thickness of the anode, electrolyte, and cathode layers was 105 μm, 53 μm, and

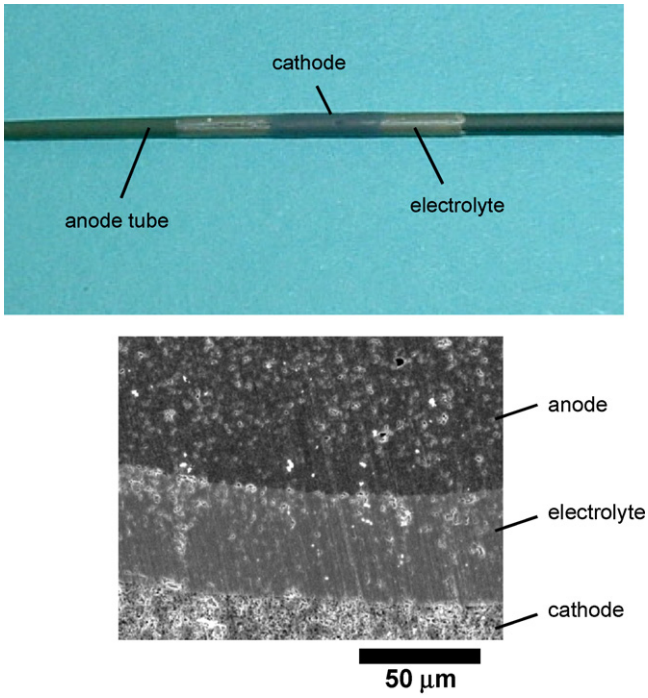

Fig. 4. Co-fired LSM–GDC/GDC/NiO–GDC microtubular cell.

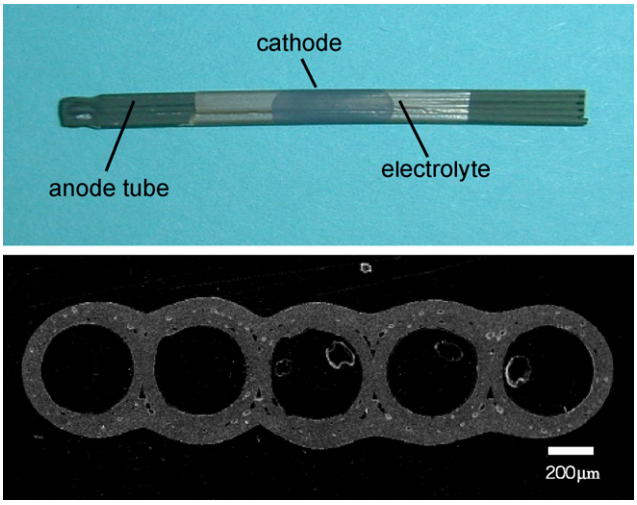

Fig. 5. Co-fired LSM–GDC/GDC/NiO–GDC microflattened ribbed cell.

20 μm, respectively. The anode gas was a humidified H_2/N_2 mixture with a flow rate of 20 ml and the cathode gas was air with a flow rate of 40 ml/min. Fig. 6 shows the performance of a co-fired LSM–GDC/GDC/NiO–GDC tubular cell. An open circuit voltage around 0.95 V at 400 °C was measured for this microtube and gradually decreased to 0.80 V at 550 °C depending upon the operating temperatures. This behavior suggests a problem with the electronic conduction of the GDC at elevated temperatures. In order to remedy this, we might consider the application of another intermediate thin layer to suppress this conduction. The maximum power density was confirmed to be around 0.14 W/cm^2 at 550 °C, a value that is comparable to that of a flat SOFC disc with the same layer composition as previously reported by considering the electrolyte thickness.[11]

The results of impedance analysis are shown in Fig. 7. Ohmic resistances of the tubular cell and the electrode at 550 °C are approximately 3.0 Ω and 13.6 Ω respectively – values that are higher than the those of other tube systems.[12,13] In this study, we selected a LSM cathode for the co-sintering of a three-layered cell. However, the microstructure and preparation conditions were not sufficiently optimized. The anode and

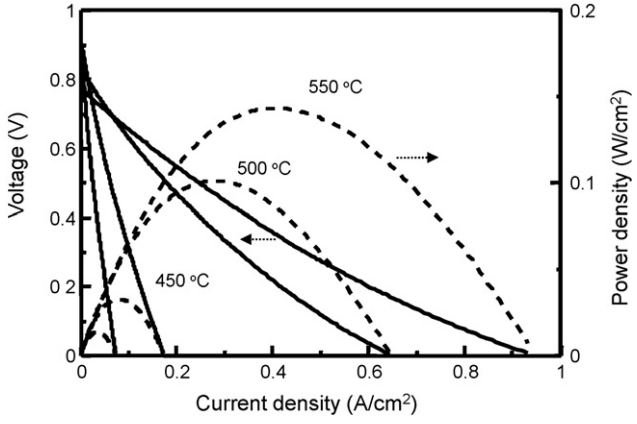

Fig. 6. Cell performance of co-fired LSM–GDC/GDC/NiO–GDC microtubular cell. Anode gas: H_2 10 ml/min + N_2 10 ml/min. Cathode gas: air 40 ml/min.

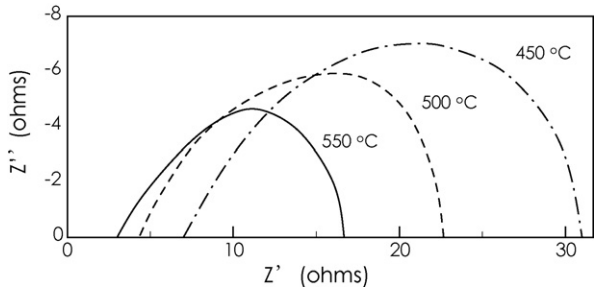

Fig. 7. Impedance spectra for the microtubular cell observed at various temperatures.

cathode fabricated by our methods are still dense compared to a sophisticated cell because no pore former was incorporated into the applied electrode slurries. Consequently, further improvements in cell performance are possible if pore formers are added to the aqueous system as outlined in the literature.[12] Further experiments are currently in progress to reduce resistance and to produce additional three-phase boundaries in both the anode and cathode through the addition of a pore former.[13,14] The thickness of the electrolyte layer is another important factor that needs to be addressed in order to reduce resistance. However, reduction in the thickness of this layer sometimes leads to a reduction in OCV by electronic conduction as reported.[15] Thus, it is desirable to prepare a high quality thinner electrolyte layer at lower temperatures to achieve higher power density without increasing electronic conduction.

Presently, it is not possible to characterize the FRCs, because manifold required to perform these measurements is not yet available. Once the microstructure of the cell has been improved, it will be characterized using the manifold designed specifically for this purpose.

4. Conclusion

This study proposes a new ceramic process for the fabrication of microtubular and flattened ribbed cells with good linearity (size accuracy). The difference in dissolution behavior in an organic solution was effectively used to make a multi-layer cell on a steel wire and the co-sintered multi-layered cell performed well as a SOFC even at 550 °C. This process can easily be automated since it is composed of simple coating and drying steps.

Further improvement of cell performance would be achieved by considering chemical reactions between the layers and microstructure of the electrodes. Tubular cells produced will subsequently be bundled for use as a smaller SOFC power unit.

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