

Short communication

Influence of patterned electrode geometry on performance of co-planar, single-chamber, solid oxide fuel cell

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Abstract

Co-planar, single-chamber, solid oxide fuel cells (SC-SOFCs) with linearly patterned electrode structures on one surface of the electrolyte are fabricated via a robo-dispensing method. The SC-SOFCs with various electrode patterns are prepared to investigate the relationship between electrode geometry and cell performance. The open-circuit voltage (OCV) for cells with a single electrode pair is unaffected by the anode-to-cathode distance. By contrast, for cells with multiple electrode pairs, increasing the number of electrode pairs leads to a gradual decrease in OCV. These observations confirm that the inter-mixing of product gases causes a loss in OCV and power density, which in turn reduces the oxygen partial pressure gradient between the anode and cathode. Keeping the electrode pairs apart by ~4 mm permits cells with complex electrode geometry to exhibit higher OCVs and power densities.

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1. Introduction

Solid oxide fuel cells (SOFCs) that directly convert chemical fuels into electricity with high efficiency are a promising clean energy sources for the future. Conventional SOFCs, generally operated at high temperatures of 600–1000 °C, are able to utilize directly hydrocarbon fuel, which makes them applicable to combined systems for residential heat and power. The high temperature operating conditions can, however, pose various problems such as long-term degradation, high costs for materials and manufacturing, and restricted cell designs. In particular, the most difficult obstacle to the commercialization of SOFCs is achieving a stable and reliable gas-tight seal between the anode and cathode gas chambers at high temperatures.

Several decades ago, Eyraud et al. [1] suggested a unique fuel cell design in which a mixture of fuel and oxidant gases was supplied to only one gas chamber, known as single chamber SOFC (SC-SOFC). More recently, Hibino et al. [2] demonstrated a remarkable electrochemical performance from SC-SOFCs

exposed to a mixture of hydrocarbon fuel and air [2]. The SC-SOFCs do not require a pore-free electrolyte or high-temperature gas-tight sealing, which allows for good thermal and mechanical shock resistance and permits a much simpler integrated cell design as the system dimension is reduced to milli- and micro-meter size ranges.

The SC-SOFCs can be largely classified into two groups according to their cell configuration. One group has the same cell configuration as conventional SOFCs where the anode and cathode are deposited on both sides of the electrolyte, while a mixed gas is fed to the cell without sealing. The other group has a patterned anode and cathode on one side of the electrolyte, denoted as co-planar SC-SOFCs, so that the ohmic resistance is reduced by the smaller gap between the anode and cathode instead of by a thin electrolyte film. This cell configuration works well for miniaturization and integration for micro-/mini-SOFCs applications. In recent years, most researches regarding SC-SOFCs had focused on the former design [3–5], whereas a few studies have been reported on the latter co-planar SC-SOFCs. Even the work related to co-planar type SC-SOFCs has been limited to basic studies that involve a simple electrode pattern composed of one anode and cathode pair [6,7], numerical calculations [8], or measurement of ionic conduction in the interdigitated electrode

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pattern [9]. To exploit fully the potential of co-planar SC-SOFCs, further in-depth research into complex electrode geometry is necessary.

In our previous work we obtained a relatively low open-circuit voltage (OCV) of ~ 350 mV for a mini-sized, co-planar SC-SOFC with micro-patterned interdigitated electrodes of 16 anode and cathode pairs [10]. We also found a decrease in the OCV depending on the complexity of the electrode geometry [11], and speculated that it was attributed to an inter-mixing of product gases evolved at both the anode and cathode as a result of the complex electrode geometry. As a result of the decrease in OCV, there is a reduction in the local oxygen concentration gradient, P_{O_2} , between the anode and cathode. To verify this assumption, we investigated the influence of electrode geometry on cell performance in co-planar type SC-SOFCs, by analyzing the effects of anode-to-cathode distance, number of electrode pairs, and electrode pair-to-pair distance. A robo-dispensing technique was used to fabricate co-planar SC-SOFCs with various complex electrode geometries [12].

2. Experimental

Co-planar SC-SOFCs with linearly patterned electrodes were fabricated using yttria-stabilized zirconia (YSZ, TZ8Y, Tosoh, Japan) as an electrolyte, $(La_{0.7}Sr_{0.3})_{0.95}MnO_3$ (LSM, Seimi, Japan)-gadolinium doped ceria (GDC, Nextech, USA) as a composite cathode, and NiO (Sumitomo, Japan)-GDC-Pd (Aldrich Chem., USA) as a composite anode. First YSZ powder was compacted by a uni-axial pressing method with a hydraulic pressure of 50 MPa using polyvinylpyrrolidone (PVP, Aldrich Chem., USA) and di-*n*-butyl phthalate (DBP, Yakuri Pure Chem. Co., Japan) as binder and plasticizer, respectively, followed by sintering at 1500 °C for 10 h. For the preparation of the anode cermet paste, NiO, GDC and Pd powders were mixed in a weight ratio of 60:37:3 and dispersed in α -terpineol-containing ethyl cellulose and dispersing agent by planetary milling at 250 rpm for 12 h. The solid loading of the anode paste was 14.8 vol.%. A cathode paste incorporating a mixture of LSM and GDC in a weight ratio of 70:30 was prepared in the same manner with a solid loading of 20 vol.%.

The anode and cathode pastes were filled in separate syringe tubes followed by extrusion through a cylindrical nozzle of 0.21 mm in diameter on to an electrolyte surface. Anode paste was dispensed under an air pressure of 1.5 torr onto the moving electrolyte disc at a speed of 1.22 mm s^{-1} to form 8 mm-long, line-shaped electrodes. After drying of the anode paste at 90 °C for 50 min, the patterned anode structure was sintered at 1350 °C for 1 h. A line-shaped cathode placed next to the anode was patterned in a similar manner followed by sintering at 1200 °C for 1 h. The resulting patterned SC-SOFCs were examined with optical microscopy (Leica DMLM) and environmental scanning electron microscopy (ESEM, FEIXL-30 FEG, Philips, Netherlands). The sintered microstructure of each electrode was investigated with an image analyzer (Leica Qwin).

After fabricating the SC-SOFCs, gold wires were attached to both ends of each line-shaped patterned electrode with gold paste (ESL Electro-Science, PA, USA) and fired at 800 °C for 1 h. For

the performance measurement, the SC-SOFC cells were placed in the middle of the quartz tube with a rectangular cross-section of ~ 28 mm in width and ~ 10 mm in height and a thermocouple was attached close to the cell placed on the alumina plate. The current–voltage (I – V) characteristics of the SC-SOFC were investigated using a dc source meter (Keithley 2425) by a current interruption method at 900 °C, while a mixture of nitrogen, methane and air in a volume ratio of 5:3:4 containing 3% H_2O at a flow rate of 240 ml min^{-1} was fed to the cell.

3. Results and discussion

The robo-dispensing method enables us to fabricate SC-SOFCs rapidly with different electrode geometric dimensions. The rheological characteristics of the pastes together with the processing conditions determine the width, height and microstructural features of the resulting line pattern [12]. Under a given dispensing condition, the width of the dispensed anode and cathode after sintering was ~ 650 and $\sim 400 \mu\text{m}$, and the thickness was 8.3 and $19.1 \mu\text{m}$, respectively. The length of the electrodes was nearly unchanged from the ~ 8 mm after sintering. The porosities of the sintered cathode and anode were 39.6 and 48.4%, respectively, based on SEM image analysis of the fractured/polished samples. As shown in Fig. 1, three types of the SC-SOFCs with different electrode patterns were prepared: the first set had only one pair of electrodes (i.e., anode and cathode) with anode-to-cathode distances of 255, 270, 443 or $783 \mu\text{m}$ (Fig. 1a), the second set had 2, 4, and 8 pairs of electrodes with a fixed anode-to-cathode distance of $\sim 300 \mu\text{m}$ (Fig. 1b), and the third set had two pairs of electrodes with pair-to-pair distances of 1.2, 5.1, or 8.0 mm (Fig. 1c).

Gas composition plays an important role in determining the cell performance of co-planar SC-SOFCs. The influence of gas composition on the OCV and cell power density at 900 °C was investigated for using the cells with a single electrode pair. Operating gases with various mixing ratios of methane and oxygen

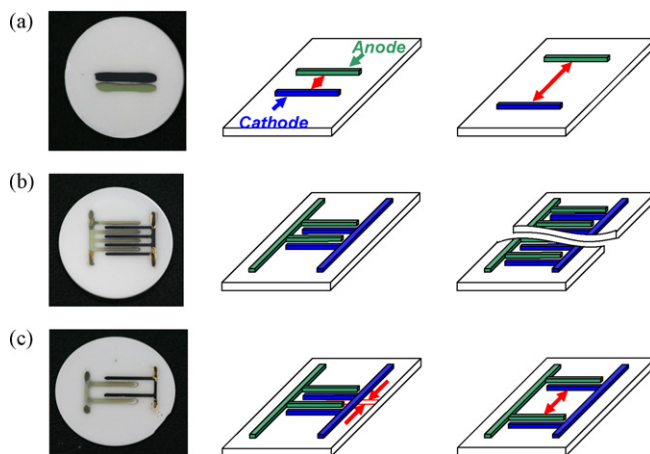


Fig. 1. Photographs and schematic illustrations showing three types of co-planar SC-SOFCs with linearly patterned electrodes on the electrolyte surface: (a) cell with single electrode pair and varying distances between anode and cathode; (b) cell with increasing numbers of electrode pairs; (c) cell with two electrode pairs and varying pair-to-pair distances.

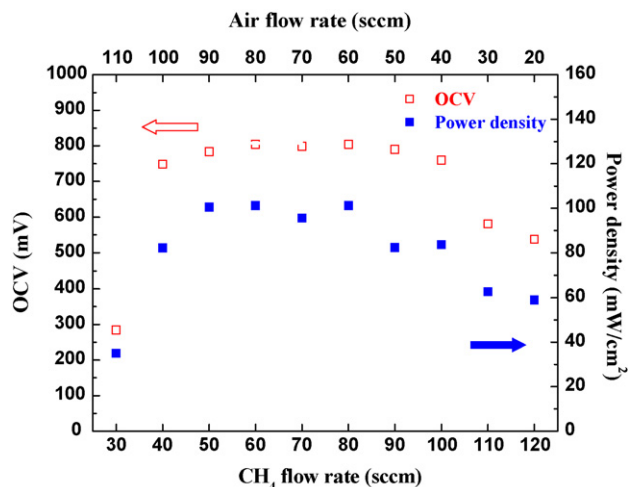


Fig. 2. Open-circuit voltage and power density of SC-SOFC with a single electrode pair and an anode-to-cathode distance of 255 μm under various gas compositions: a methane flow rate varying from 20 to 120 sccm while the total flow rate of methane and air together with nitrogen carrier gas of 100 sccm was kept to 240 sccm.

were fed to the cells, while the total amount of methane and air together with nitrogen carrier gas at 100 sccm was fixed at 240 sccm. Better cell performance is observed in the range of 50–80 sccm of methane flux, where the molar ratio of methane to oxygen, referred to as R_{mix} , is in the range of 2.78–6.67, as shown in Fig. 2. The maximum OCV and power density are 804 mV and 101.2 mW cm^{-2} , when 60 sccm of methane, 80 sccm of air, and 100 sccm of nitrogen (i.e., at the condition of $R_{\text{mix}} = 3.75$) are supplied. The maximum OCV, however, is lower than the theoretical value derived from the Nernst equation. Furthermore, the best cell performance is obtained at a value of R_{mix} that is relatively higher than the stoichiometric ratio of methane to oxygen required for partial oxidation of methane (i.e., $R_{\text{mix}} = 2$) [13]. This implies the existence of a parasitic reaction, which does not produce fuel gases required for SC-SOFC operation, but rather consumes methane. Such a phenomenon can be due to: (i) the methane combustion resulting from the presence of GDC and Pd in the anode, which are added to prevent carbon deposition and to promote the partial oxidation of methane, or (ii) the steam reforming of methane under wet gas containing 3% H_2O .

Doped ceria material such as GDC and Pd are typical catalysts for the oxidation of hydrocarbon fuel, so that direct chemical reaction of methane (Eq. (1)) can occur locally around the anode area at the high operating temperature, as described by Riess [14].



In the present experiment, nitrogen carrier gas is necessary to develop the OCV for the NiO-GDC-Pd cermet anode, while the NiO-YSZ cermet anode exhibits an OCV of ~ 800 mV without N_2 gas. This observation supports the existence of direct methane combustion since nitrogen gas acts as a diluent for OCV development in the NiO-GDC-Pd cermet anode. Such a methane combustion reaction produces CO_2 and H_2O by con-

suming CH_4 and O_2 , so that the fuel concentration of H_2 and CO around the anode decreases, resulting in a lower OCV than theoretical values. The methane combustion reaction, however, is not thought to cause a higher R_{mix} because there is more oxygen consumed than methane in the reaction, as shown in Eq. (1).

Steam reforming of methane is likely to be responsible for the higher R_{mix} and the lower than theoretical OCV values. Conversion of methane to hydrogen and carbon monoxide is mainly achieved by the two reactions: steam reforming and partial oxidation by oxygen, i.e.,



Methane partial oxidation (Eq. (3)) is known to be exothermic, while steam reforming is endothermic (Eq. (2)). Thus, it is typical to observe an increase in local temperature close to the anode [15]. When dry mixed gas is supplied to the SC-SOFC, the measured temperature difference between the inside and outside reaction chamber is much higher ($\Delta T \sim 20^\circ\text{C}$) than when wet gas is supplied ($\Delta T \sim 3^\circ\text{C}$). The lower rise in temperature with wet gas operation is indicative of the steam reforming reaction, which simultaneously occurs to some extent in the presence of vapour, and absorbs the heat generated by the partial oxidation of methane. We have confirmed that the maximum cell performance with a higher OCV is obtained at a theoretically optimized value ($R_{\text{mix}} = 2.0$), with a stoichiometric methane-to-oxygen ratio for methane partial oxidation (Eq. (3)), under dry mixed-gas conditions. Under wet mixed-gas conditions, steam reforming requires more methane, which results in a higher R_{mix} of about 3.75.

Stefan et al. [16] have suggested that the gas flow direction relative to the anode and cathode orientation in the SC-SOFC is also a significant determinant of cell performance. Thus, we also tried to determine how the gas flow direction influences the performance of coplanar type SC-SOFCs with a single pair of linear electrodes. Three different cell configurations with respect to gas flow orientation were tested namely, parallel to gas flow (Fig. 3a), and perpendicular to gas flow with either cathode (Fig. 3b) or anode (Fig. 3c) placed ahead. The measured OCV of the cell as a function of gas flow orientation at 900°C is presented in Fig. 3d as the R_{mix} is varied from 1 to 5. For all values in the R_{mix} range, the OCV is lowest in cells where the anode met the mixed gas first. The highest OCV is obtained for cells in which linear electrodes were placed in a parallel direction to the gas flow. A lower OCV for cells with a perpendicular gas flow configuration could be due to a lower oxygen partial pressure gradient between the anode and cathode as a result of the inter-mixing of intermediate and/or final product gases after the electrocatalytic reaction in each electrode. In particular, a cell in which the anode meets the mixed gas first in a perpendicular manner suffers from almost a zero gradient in the oxygen partial pressure. The oxygen could be nearly consumed at the anode placed ahead of the cathode by methane partial oxidation, which, in turn, prevents the cell from developing a high OCV. By contrast, the cell in a parallel gas flow configuration confronts less inter-mixing and thereby develops the highest OCV.

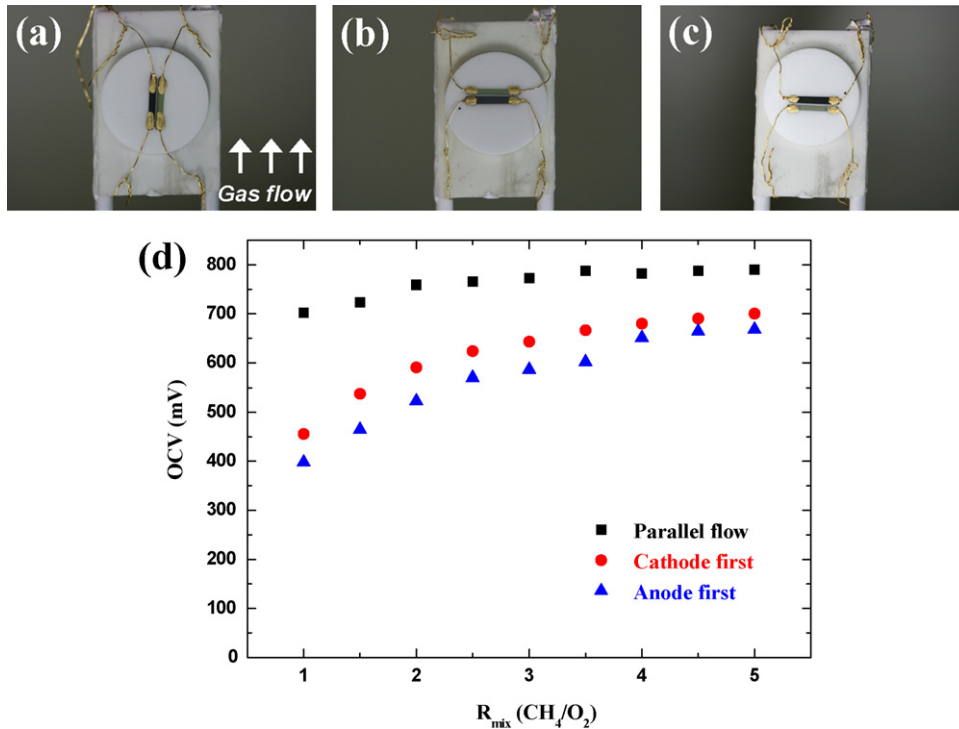


Fig. 3. Three different cell configurations with respect to gas flow orientation: (a) parallel to gas flow; (b) perpendicular to gas flow while the cathode is placed ahead; (c) perpendicular to gas flow while the anode is placed ahead; and (d) measured OCVs for each cell configuration at 900°C as a function of fuel/oxidant mixing molar ratio (R_{mix}).

Further analysis of the influence of electrode geometry on cell performance was performed at 900°C in the parallel gas flow configuration using a wet mixed gas of $R_{\text{mix}} = 3.75$. The OCV and power density of the SC-SOFCs with a single electrode pair with varying anode-to-cathode distances are shown in Fig. 4. Although the anode-to-cathode distance varied from 255 to $783\ \mu\text{m}$, the OCV shows little variation (804, 820, 790, and $782\ \text{mV}$). The OCV is nearly independent of the anode-to-cathode distance within the investigated length range. It is possible, however, that the OCV decreases as the anode-to-cathode distance becomes narrower than $255\ \mu\text{m}$, due to the

increased possibility of product gas inter-mixing. The power density of the SC-SOFCs linearly decreases from 101.2 to 90.5 to 80.2 to $55.6\ \text{mW cm}^{-2}$ with increasing anode-to-cathode distance, as similarly observed by Hibino et al. [6,7]. Increase in the anode-to-cathode distance in the co-planar SC-SOFCs prolongs the diffusion path of the oxygen ion and this results in an increase in the ohmic resistance.

The variation in the OCV of co-planar SC-SOFCs with a varying number of electrode pairs is presented in Fig. 5. The OCVs for SC-SOFCs with the 1, 2, 4 and 8 pairs of electrodes

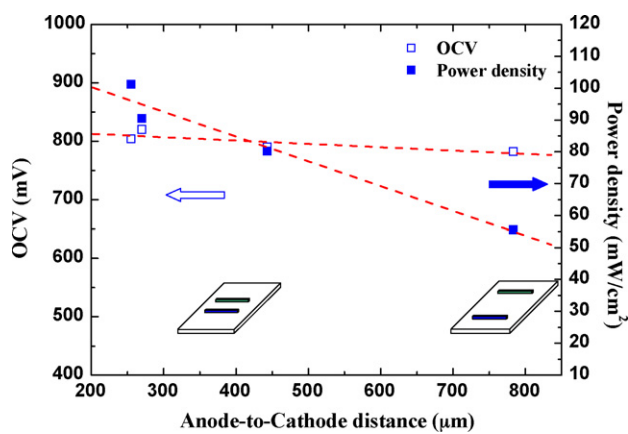


Fig. 4. Open-circuit voltage and power density of SC-SOFC with a single electrode pair and varying anode-to-cathode distances at 900°C using a wet mixed gas of $R_{\text{mix}} = 3.75$.

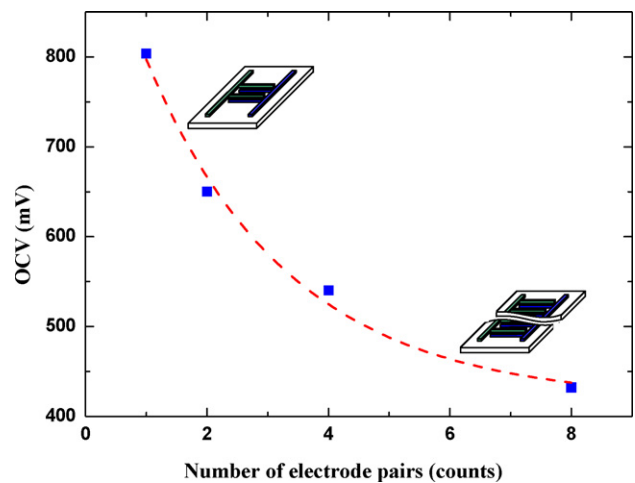


Fig. 5. Open-circuit voltage drop for SC-SOFCs with multiple electrode pairs as a function of number of electrode pairs at 900°C using wet mixed gas of $R_{\text{mix}} = 3.75$.

at a fixed anode-to-cathode distance of $\sim 250 \mu\text{m}$ are 804, 650, 540 and 432 mV, respectively. The OCV decreases with increasing complexity of the electrode geometry, which is consistent with the findings from our previous work. The microfluidically patterned SC-SOFC with 16 pairs of electrodes and an anode-to-cathode distance of $50 \mu\text{m}$ exhibits a relatively low OCV of about 350 mV [10]. For an ideal SC-SOFC, the operation mechanism is the same as for a conventional SOFC, in which the partial oxidation of the methane needs to occur only at the anode and the oxygen is reduced only at the cathode [17]. The selective partial oxidation and reduction induces a difference in the oxygen partial pressure between the anode and cathode, which is the driving force for fuel cell operation with a maximized OCV. In this regard, the decrease from the theoretically calculated OCV can be attributed to a loss in the oxygen partial pressure between the electrodes, which can be caused by various reasons.

As previously stated, the partial oxidation of the methane on the anode is always accompanied by strong heat evolution [15], and the anode has higher a local temperature than the cathode. Although the thermocouple placed on the bottom of the cell measured a very small temperature difference ($\sim 3^\circ\text{C}$) due to the steam reforming, the actual local temperature rise on the anode should be much larger. Furthermore the SC-SOFC operation under a wet gas condition entails steam reforming and partial oxidation reaction of methane, both of which are characterized by molar volume expansion reactions as indicated in Eqs. (2) and (3). A large volume expansion is expected to occur locally at the anode at 900°C , which sets up a pressure difference between the anode and cathode. These local temperature and pressure gradients across the electrodes can induce both the convection flow and mass transport by which the product gases of CO and H_2 at the anode are transferred towards the cathode and oxidized with O_2 [18]. Such an intermixing of the fuel gas at the electrode becomes more serious with an increased number of electrode pairs of closely packed anodes and cathodes. Placing many electrode pairs on the electrolyte causes the product gases to be more exposed to the anode-facing-cathode site where direct fuel combustion occurs. This effect is manifested by a gradual decrease in the OCV, as shown in Fig. 5.

The OCVs and I - V characteristics for the SC-SOFCs with two electrode pairs that vary in inter-pair spacing are summarized in Fig. 6a and b. The OCV increases from 650 to 807 mV as the distances between the electrode pairs increased from 0.3 to 8.0 mm. The OCV values are 805 and 807 mV for a pair-to-pair distance of 5.1 and 8.0 mm, respectively, which is similar to the OCV for an SC-SOFC with a single electrode pair. The dotted line in Fig. 6a represents the tendency of the OCV to change as a function of the pair-to-pair distance. The OCV shows a limit of ~ 800 mV when the pair-to-pair distance reaches ~ 4 mm. This suggests that increasing the distance between electrode pairs prevents the product gases from being inter-mixed, which enables each electrode pair to maintain a large oxygen difference in partial pressure that results in the recovery of OCV.

The I - V characteristics of the SC-SOFCs as a function of the pair-to-pair distance also exhibit a unique behaviour

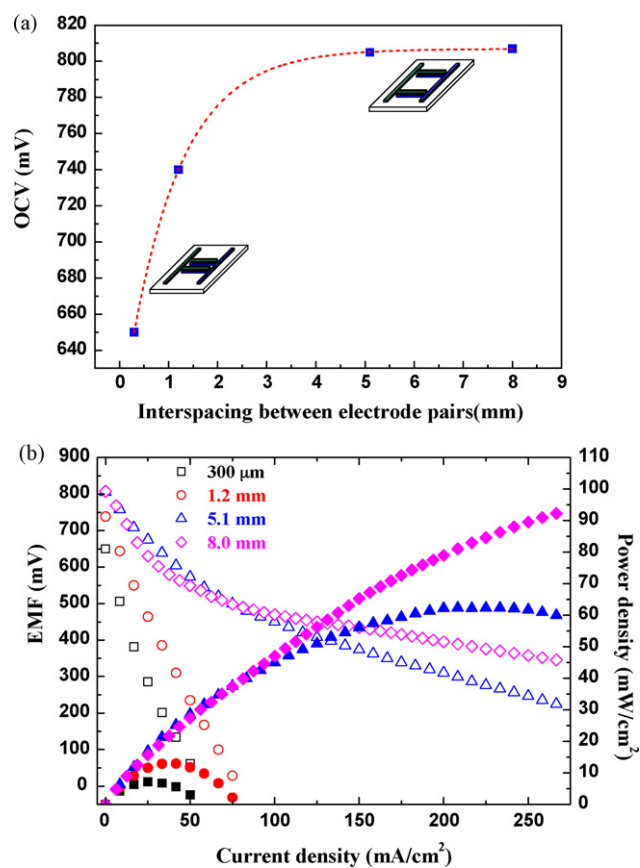


Fig. 6. (a) Open-circuit voltage variation and (b) performance of SC-SOFCs with two electrode pairs and varying pair-to-pair distance at 900°C using wet mixed gas of $R_{\text{mix}} = 3.75$.

(Fig. 6b). The SC-SOFCs with a narrow pair-to-pair distance (0.3–4 mm) experiences an abrupt voltage drop, while the cell with a wider pair-to-pair distance (>5 mm) displays a gentle slope. The variation of I - V slope as a function of electrode pair distance is related to the oxygen deficit-induced cathodic polarization caused by direct fuel combustion at the cathode. When the pair-to-pair distance is up to ~ 4 mm, the power densities are comparable with the value for a cell with a single electrode pair (i.e., 60 – 100 mW cm^{-2}). Further reduction in the inter-electrode pair distance, however, drastically decreases the power density to $\sim 10 \text{ mW cm}^{-2}$. These findings on the influence of electrode geometry indicated that co-planar SC-SOFCs with multiple electrode pairs may not be suitable for maximized cell performance with high OCV, unless the pair-to-pair distance is sufficiently larger than 4 mm under wet mixed-gas condition. It is necessary to introduce a barrier structure between the electrode pair in order to suppress the inter-mixing of product gases. It should be noted, however, that a SC-SOFC operating in dry gas at lower temperature will eliminate the undesirable steam reforming reaction. The reduction in individual electrode size will minimize the temperature and pressure gradients across the anode and cathode. On fulfillment of these conditions, even SC-SOFCs with multiple electrode pairs might develop a relatively high OCV.

4. Conclusions

The influence of electrode geometry on the performance of co-planar SC-SOFCs, has been investigated. A maximum OCV and power density are obtained at 900 °C when using a wet mixed gas of $R_{\text{mix}} = 3.75$ in a parallel gas flow configuration with respect to the electrode direction. The SC-SOFC with a single electrode pair exhibits uniform OCVs in the range of 782–804 mV with decreasing anode-to-cathode distance, but the power density increases due to a decrease in ohmic resistance. For cells with multiple electrode pairs, the OCV drastically decreases with an increasing number of closely patterned electrode pairs because of the effect from inter-mixing of product gases. Such a decrease in OCV could be suppressed by increasing the inter-electrode pair distance. The electrode geometry restriction associated with co-planar type SC-SOFCs must be solved before use of SC-SOFCs for mini- and/or micro-scale portable power generation.

Acknowledgements

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